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<b>(54) Title:</b> HIGH LATHER STYLING SHAMPOOS  <b>(57) Abstract</b>  The present invention relates to hair shampoo compositions which have improved cleansing, lathering, and styling benefits. These shampoo compositions comprise an alkyl glyceryl ether sulfonate surfactant, a hair styling polymer, a non-polar volatile solvent, and water. These compositions are useful for cleansing the hair and for providing a hair styling benefit.		

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## HIGH LATHER STYLING SHAMPOOS

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### TECHNICAL FIELD

The present invention relates to hair shampoo compositions which have improved cleansing, lathering, and styling benefits. These shampoo compositions  
10 comprise an alkyl glyceryl ether sulfonate surfactant, optionally in combination with one or more additional surfactants. These compositions also comprise a hair styling polymer which is incorporated in a non-polar volatile solvent, which are together dispersed in the shampoo composition. Preferred embodiments of the present invention additionally comprise a hair conditioning agent. These preferred  
15 embodiments provide hair cleansing, styling, and conditioning benefits from a single product.

### BACKGROUND OF THE INVENTION

In washing, drying and styling one's hair, several end results are desired. Firstly, and most obviously, one desires that the hair be thoroughly cleansed. Most  
20 desirable is a hair care process which maintains the look and feel of clean hair between hair washings.

Also, one desires a hair care process or product that provides hair styling benefits, especially hair style achievement and hold. Such style retention is generally accomplished by either of two routes: permanent chemical alteration or  
25 temporary alteration of hair style and shape. A permanent alteration, for example a chemical perm, involves the use of chemical agents to react with the hair in order to achieve the desired effect. This permanent chemical alteration of the hair, however, is not an object of the present invention. The styling benefit provided by the present invention is a temporary alteration. A temporary alteration is one which can be  
30 removed by water or by shampooing. In other words, it is a non-permanent alteration.

Temporary style alteration has generally been accomplished by means of the application of a separate composition or compositions after the shampooing process to provide style achievement and hold of hair. The materials used to provide these  
35 temporary styling benefits have generally been resins or gums that are usually applied in the form of mousses, gels, lotions, or sprays. This approach presents several significant drawbacks to the user. It requires a separate step following shampooing to apply the styling composition. In addition, many of these styling agents are aesthetically unappealing, leaving the hair feeling sticky or stiff after

application of the styling composition, thereby defeating the purpose of the cleansing process. Moreover, many styling agents do not provide a long-lasting style benefit or provide a styling benefit that is too easily disturbed.

While the shampoo compositions that are disclosed in the prior art provide  
5 cleansing and conditioning benefits, they do not provide effective styling benefits. The benefits derived from styling are highly desirable. However, styling agents, such as styling polymers, cannot be readily incorporated into conventional shampoos without suppressing the lathering and cleansing ability of the shampoos, or the ultimate deposition and performance of the styling polymer.

10 In the present invention, it has surprisingly been found that certain surfactant systems such as alkyl glyceryl ether sulfonates can provide high cleansing and lathering properties in a system also containing a styling polymer. Furthermore, it has been found that when the styling polymer is dissolved in a non-polar volatile solvent that the styling polymer is readily dispersed in the shampoo composition and  
15 that the polymer is deposited onto the hair during the cleansing and rinsing process. Previous developments in this area employed a styling polymer dissolved in a polar solvent, which was emulsified into a shampoo base. See U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1993, which is incorporated by reference herein in its entirety. Polar solvents, however, can inhibit the deposition of the styling polymer.  
20 These solvents tend to be too soluble in the shampoo base, and can carry the styling polymer into the water phase of the shampoo and away from the hair into the the rinse water during the rinsing process. In addition, many of the commonly used polar solvents have strong objectionable odors or may be hydrolytically unstable in an aqueous environment. A non-polar solvent would be preferable in such  
25 instances, however, non-polar solvents tend to interfere with the cleansing and lathering ability of the surfactant base of the shampoo. Typical high lathering surfactants such as alkyl sulfates can build lather in the presence of non-polar solvents, but have the disadvantage of reducing deposition so that no styling benefit is achieved. Alkyl glyceryl ether sulfonates are also known to be good lathering  
30 surfactants. See U.S. Patent No. 2,979,465, to Parran et al., issued April 11, 1961, which is incorporated by reference herein in its entirety. It has, however, surprisingly been found that alkyl glyceryl ether sulfonate surfactants are able to produce good cleansing and lathering without interfering with the deposition of a hair styling polymer dissolved in a non-polar volatile solvent.

35 The present invention relates to hair shampoo compositions which comprise an alkyl glyceryl ether sulfonate surfactant, a hair styling polymer, a non-polar volatile solvent for dissolving the polymer, and water. Shampooing with these

products provides both hair cleansing and styling benefits from a single product. These compositions also have good lathering ability. It has also been discovered that when a hair conditioning agent is added to the aforementioned product, hair conditioning, cleansing, and styling benefits can be achieved from a single hair care product. It has also been discovered that the styling shampoo compositions of the present invention provide product viscosities that maintain product phase stability and a consumer pleasing aesthetic appearance.

It is therefore an object of the present invention to provide hair shampoo compositions which provide both effective hair cleansing and good styling properties from a single composition.

It is also an object of the present invention to provide hair shampoo compositions which provide good lathering ability.

It is also an object of the present invention to formulate hair shampoo compositions which provide good style retention benefits without leaving the hair with a stiff, sticky, or tacky feel.

It is also an object of the present invention to formulate hair shampoo compositions which also provide effective conditioning properties.

It is also an object of the present invention to provide an improved method for cleansing and styling the hair.

These and other objects will become readily apparent from the detailed description which follows.

#### SUMMARY OF THE INVENTION

The present invention relates to a lathering, hair styling shampoo composition comprising:

(a) from about 2% to about 25%, by weight, of an alkyl glyceryl ether sulfonate surfactant;

(b) from about 0.1% to about 10%, by weight, of a hair styling polymer;

(c) from about 0.1% to about 10%, by weight, of a non-polar volatile solvent for solubilizing said hair styling polymer, said non-polar volatile solvent having a boiling point of less than or equal to about 300°C, and a solubility in water at 25°C of less than about 0.2% by weight; and

(d) from about 50% to about 97.8% water;

wherein the weight ratio of said hair styling polymer to said non-polar volatile solvent is from about 10:90 to about 70:30.

The present invention also relates to methods for cleansing and styling the hair utilizing the compositions of the present invention. These methods comprise the steps of:

- (i) wetting the hair with water,
- (ii) applying an effective amount of the shampoo composition to the hair,
- (iii) shampooing the hair with said composition,
- (iv) rinsing said composition from the hair, and
- 5 (v) drying and styling the hair.

All percentages and ratios used herein are by weight of the total composition and all measurements made are at 25°C or room temperature, unless otherwise designated. All weight percentages, unless otherwise indicated, are on an actives weight basis. The invention hereof can comprise, consist of, or consist essentially of, the essential as well as the optional ingredients and additional components  
10 described herein.

#### DETAILED DESCRIPTION OF THE INVENTION

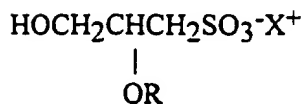
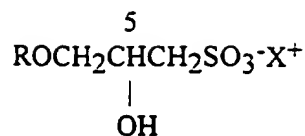
The styling polymers and non-volatile solvents of the present invention can be used in a wide variety of hair styling products, including shampoos, hair sprays,  
15 hair lotions, hair tonics, hair mousses, and hair rinses.

The essential, as well as the optional, components of the present invention are described below.

#### Alkyl Glyceryl Ether Sulfonate Surfactant

The compositions of the present invention comprise an alkyl glyceryl ether  
20 sulfonate surfactant (also referred to herein as an "AGS" surfactant) as the cleansing and lathering ingredient. These compositions comprise from about 2% to about 25%, more preferably from about 3% to about 20%, and most preferably from about 4% to about 10% of the alkyl glyceryl ether sulfonate surfactant. These AGS surfactants are derived from an alkyl glyceryl ether containing a sulfonate or  
25 sulfonate salt group. These compounds generally can be described as an alkyl monoether of glycerol that also contains a sulfonate group.

These AGS surfactants can be described as generally conforming to the following structures:



wherein R is a saturated or unsaturated straight chain, branched chain, or cyclic alkyl group having from about 10 to about 18 carbon atoms, preferably from about 11 to about 16 carbon atoms, and most preferably from about 12 to about 14 carbon atoms, and X is a cation selected from the group consisting of ammonium; mono-alkylsubstituted ammonium; di-alkylsubstituted ammonium; tri-alkylsubstituted ammonium; tetra-alkylsubstituted ammonium; alkali metal; alkaline metal; and mixtures thereof. More preferably, the alkyl radicals, R in the above formulas, are saturated and straight chain.

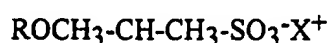
The distribution of alkyl chain lengths in the AGS surfactant has some effect on the character of the overall shampoo product. A satisfactory distribution can be achieved in a commercially practicable way by using fatty alcohols derived from coconut oil and tallow. An equivalent distribution of alkyl chain lengths can be achieved using other starting materials. In the preparation of the coconut fatty alcohols used to provide the alkyl group of the AGS, preferably the middle cut of the coconut oil is taken. The higher boiling cut can be retained with the middle cut coconut oils if desired. In the preparation of the tallow fatty alcohols, a hydrogenation step is included to insure that they are substantially saturated.

The preferred AGS compounds are those where the alkyl group is derived from at least about 50% from alcohols of about 10 to about 18 carbons, having mainly monoglyceryl radicals present, with less than about 30% of diglyceryl radicals present. The AGS used in the Examples described below contains about 15% of diglyceryl ether sulfonates, and is preferred because of the ease of manufacturing this material. The term "AGS" is intended to include monoglyceryl, diglyceryl, and traces of the higher glyceryl compounds. Small amounts, that is less than about 3% total, of triglyceryl ether sulfonates and tetraglyceryl ether sulfonates can be present. Also included are AGS's derived from glyceryl ethers having branched or mixed branched and straight chain lengths that emulate the straight chain lengths.

The more preferred AGS surfactants for use in this invention are those which have a C<sub>12-14</sub> straight chain length, and are crystalline in structure. The preferred

cation, "X", in the AGS surfactants is sodium. An example of a commercially available AGS surfactant useful herein includes sodium cocoglyceryl ether sulfonate, as listed in CTFA International Cosmetic Ingredient Dictionary, fifth edition, 1993, page 660, which is incorporated by reference herein in its entirety.

The AGS surfactants of this invention can be prepared using a variety of standard synthetic methods. The AGS surfactants can be preferably prepared by reacting fatty alcohols with a slight excess of epichlorohydrin, and then sulfonating the resulting chloroglyceryl ethers by means of the Streckerization Reaction. Secondary reaction products, such as alkyl diglyceryl ether disulfonates,



are formed in addition to the alkyl monoglyceryl ether sulfonate which is the primary product. Additional isomers of the diglyceryl compound are also formed and can be monosulfonated or disulfonated. For the purposes of this invention, the sodium alkyl glyceryl ether sulfonate should contain less than about 30% of the diglycerol ether product, and preferably less than about 25%. The balance is substantially monoglyceryl ether sulfonate. Generally, it is not desirable to reduce the alkyl diglyceryl ether content below about 5% for economic reasons.

The AGS surfactants useful in the present invention are more fully described in U.S. Patent No. 2,979,465, to Parran et al., issued April 11, 1961; U.S. Patent No. 3,179,599, to Eaton et al., issued April 20, 1965; British Patent No. 848,224, published Sept. 14, 1960; British Patent No. 791,415, published March 5, 1958; U.S. Patent No. 5,322,643, to Schwartz et al., issued June 21, 1994; and U.S. Patent No. 5,084,212, to Farris et al. issued Jan. 28, 1992; which are all hereby incorporated herein by reference in their entirety. These references also disclose various cleansing products in which the AGS surfactant of this invention can be used.

#### Hair Styling Polymer

The shampoo compositions of the present invention comprise a hair styling polymer. It is this component that provides the hair styling benefits to the user. The compositions of the present invention comprise from about 0.1% to about 10%, more preferably from about 0.3% to about 7%, and most preferably from about 0.5% to about 5% of the styling polymer.

A wide variety of hair styling polymers are known for use as styling agents. Many homopolymers, copolymers, and polymers combining three or more different



monomer units are known in the art. Examples of such complex polymer systems are found in U.S. Patent 5,120,531, to Wells et al., issued June 9, 1992; U.S. Patent 5,120,532, to Wells et al., issued June 9, 1992; U.S. Patent 5,104,642, to Wells et al., issued April 14, 1992; U.S. Patent 4,272,511, to Papantoniou et al., issued June 9, 1981; and U.S. Patent 4,196,190, to Gehman et al., issued April 1, 1980, all of which are incorporated by reference herein in their entirety.

The polymers used herein are hydrophobic, water insoluble polymers. These polymers contain monomer units derived from polymerizable hydrophobic monomers. The term "hydrophobic monomer" means a monomer, that upon polymerization with like monomers, forms a water-insoluble homopolymer. The polymers can contain other monomer units which are not hydrophobic, however the polymer must remain water-insoluble as defined above.

The term "water-insoluble" polymer or homopolymer means a polymer that has a solubility in water at 25°C of about 0.2% or less, calculated on a water plus polymer weight basis. "Solubility" for purposes hereof corresponds to the maximum concentration of polymer that can dissolve in water to form a solution that is substantially clear to the naked eye, as is well understood to those skilled in the art.

The hair styling polymer preferably has a glass transition temperature, T<sub>g</sub>, i.e., the temperature at which the polymer changes from a brittle vitreous state to a plastic state, of at least about -20°C, preferably between about 0°C and about 80°C, and most preferably between about 20°C and about 60°C. T<sub>g</sub> can be determined by differential scanning calorimetry, a method well known to one skilled in the art.

The hair styling polymers of the present invention have a weight average molecular weight of at least about 10,000. The molecular weight will generally be less than about 5,000,000, although higher molecular weights are not intended to be excluded. Preferably, the weight average molecular weight will be from about 30,000 to about 5,000,000, more preferably at least about 50,000, even more preferably at least about 75,000. The weight average molecular weight is preferably less than about 200,000, more preferably less than about 150,000. Weight average molecular weight, for purposes hereof, can be measured by methods known in the art suitable for determining the molecular weight of the sample to be analyzed, for example size exclusion chromatography utilizing column pore sizes of 10<sup>3</sup>, 10<sup>5</sup>, and 10<sup>6</sup> angstroms, or other equivalent methods.

Suitable hydrophobic monomers include acrylic or methacrylic acid esters of C<sub>1</sub>-C<sub>18</sub> alcohols, such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 3-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-

methyl-1-pentanol, *t*-butanol, cyclohexanol, neodecanol, 2-ethyl-1-butanol, 3-heptanol, benzyl alcohol, 2-octanol, 6-methyl-1-heptanol, 2-ethyl-1-hexanol, 3,5-dimethyl-1-hexanol, 3,5,5-trimethyl-1-hexanol, 1-decanol, and the like, the alcohols having from about 1-18 carbon atoms with the average number of carbon atoms being from about 4-12; vinyl acetate; vinyl chloride; vinylidene chloride; vinyl propionate; butadiene; cyclohexadiene; ethylene; propylene; vinyl toluene; and methoxy ethyl methacrylate. The polymers hereof can be homopolymers of such hydrophobic monomers or can be co-, ter-, and other higher polymers of hydrophobic monomers.

10 Preferred monomers include *n*-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, *t*-butylacrylate, *t*-butylmethacrylate, and mixtures thereof. Especially preferred are *t*-butylacrylate, *t*-butylmethacrylate, and 2-ethylhexyl methacrylate.

The polymers hereof can be made by conventional polymerization techniques well known in the art including, for example, free radical polymerization.

Preferred examples of polymers useful in the present invention include the following: *t*-butyl acrylate/2-ethylhexyl acrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl methacrylate/2-ethylhexyl acrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl methacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl ethacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; and mixtures thereof.

Especially preferred polymers are *t*-butyl acrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; *t*-butyl methacrylate/2-ethylhexyl methacrylate copolymers having a weight/weight ratio of monomers of about 95/5, about 90/10, about 80/20, about 70/30, about 60/40, and about 50/50; and mixtures thereof.

#### Non-Polar Volatile Solvent

The compositions of the present invention also comprise a non-polar volatile solvent or diluent for the styling polymer. The solvent is useful for diluting and solubilizing the polymer so that it can be dispersed as fluid particles in the shampoo composition. The amount of solvent to be used in the present shampoo

compositions is an amount sufficient to solubilize the polymer and disperse it as a separate fluid phase in the shampoo composition. The compositions of the present invention comprise from about 0.10% to about 10%, preferably from about 0.5% to about 8%, and most preferably from about 1% to about 6% by weight of the polymer solvent. At levels below about 0.1% solvent, the polymer generally cannot be sufficiently diluted; while at levels above about 10% solvent, the shampoo's cleansing and lathering characteristics can be negatively affected. The weight/weight ratio of polymer to solvent in the present composition is from about 10:90 to about 70:30, preferably from about 30:70 to about 60:40.

Without being limited by theory, the solvent also aids in delivering style achievement by plasticising the polymer deposited on the hair, thereby making it more flexible and adhesive during the hair drying and styling process. Furthermore, the solvent should have a low solubility in water. Most preferred are the hydrocarbons which have a solubility in water of less than about 0.5% by weight, preferably less than 0.3% by weight, and most preferably less than 0.2% by weight. The particular polymer chosen for use in the present shampoo compositions must be soluble in the particular solvent utilized, thereby allowing the dispersion of the polymer and solvent mixture as a dispersed fluid phase in the shampoo composition.

Additionally, the solvents must not interact with the polymer styling agent in such a way that would substantially reduce the ability of the polymer to provide styling benefits to the hair under ordinary use situations. The solvents must, of course, be of sufficiently high purity and sufficiently low toxicity to render them suitable for administration to human hair.

The polymer solvent must also be volatile. Upon deposition of the polymer and solvent mixture onto the hair, the solvent is volatilized leaving only the styling polymer on the hair, thus providing the maximum styling benefits. Generally, the polymer solvents of the present invention have a boiling point of less than or equal to about 300°C, more preferably from about 90°C to about 260°C, and most preferably from about 100°C to about 200°C.

The volatile solvents useful in the present compositions can be hydrocarbons, ethers, or mixtures thereof. Most preferred are the hydrocarbons, especially the C<sub>10</sub>-C<sub>16</sub> branched chain hydrocarbons. The most preferred solvents for use herein are isohexadecane, isododecane, 2,5-dimethyl decane, and mixtures thereof.

The hydrocarbons may be either straight or branched chain and may contain from about 8 to about 18 carbon atoms, preferably from about 10 to about 16 carbon atoms. Saturated hydrocarbons are preferred, although it is not necessarily intended

to exclude unsaturated hydrocarbons. Examples of suitable straight chain hydrocarbons are decane, dodecane, decene, tridecene, and mixtures thereof. Suitable branched chain hydrocarbons include isoparaffins of the above chain lengths. Isoparaffins are commercially available from Exxon Chemical Co. Examples include Isopar™ H and K (C<sub>11</sub>-C<sub>12</sub> isoparaffins), and Isopar™ L (C<sub>11</sub>-C<sub>13</sub> isoparaffins). Other suitable branched chain hydrocarbons are isododecane and isohexadecane. These solvents are commercially available from Preperse, Inc. (South Plainfield, NJ, USA) as Permethyl™ 99A and 101A, respectively. Useful ethers include di(C<sub>5</sub>-C<sub>7</sub>) alkyl ethers and diethers, especially the di(C<sub>5</sub>-C<sub>6</sub>) alkyl ethers such as isoamyl ether, dipentyl ether and dihexyl ether.

The most preferred volatile solvents hereof are the hydrocarbons.

#### Hair Styling Agent

The mixture of hair styling polymer and non-polar volatile solvent used in the present compositions is also referred to herein as the styling agent. The hair styling agent of the present invention comprises a mixture of a water-insoluble, hydrophobic hair styling polymer and a water-insoluble, non-polar volatile diluent.

The hair styling agent generally should have a hair styling polymer to volatile solvent weight ratio of from about 10:90 to about 70:30, preferably from about 20:80 to about 65:35, and more preferably from about 30:70 to about 60:40. The hair styling polymer is admixed with the non-polar volatile solvent, preferably in a weight ratio of from about 10:90 to about 70:30, more preferably from about 20:80 to about 65:35, and most preferably from about 30:70 to about 60:40. If the ratio of polymer to solvent is too low, the lathering performance of the shampoo composition is negatively affected. If the ratio of polymer to solvent is too high, the composition becomes too viscous and causes difficulty in the dispersion of the styling polymer. The hair styling agents should have an average particle diameter in the final shampoo product of from about 0.1 to about 100 microns, preferably from about 0.5 micron to about 25 microns. Particle size can be measured according to methods known in the art, including, for example optical microscopy.

Preferred examples of hair styling agents include the following materials. It should be noted that the numbers in parentheses following the polymers indicates the relative weight ratios of the monomers.

#### **Mixture A.**

	w/w ratio
Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (90/10w/w)	40
Solvent: isododecane	60

#### **Mixture B.**

Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (90/10w/w)	50
Solvent: isododecane	50

**Mixture C.**

Polymer: t-butyl methacrylate/2-ethylhexyl methacrylate (50/50w/w)	40
Solvent: isohexadecane	60

**Mixture D.**

Polymer: t-butyl methacrylate/2-ethylhexyl methacrylate (50/50w/w)	30
Solvent: Isoparaffin Blend (C <sub>11</sub> -C <sub>12</sub> ) <sup>1</sup>	70

**Mixture E.**

Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (60/40w/w)	40
Isoparaffin Blend (C <sub>11</sub> -C <sub>13</sub> ) <sup>2</sup>	60

<sup>1</sup> Sold as Isopar H by Exxon, which is a mixture of C<sub>11</sub>-C<sub>12</sub> isoparaffins.

<sup>2</sup> Sold as Isopar L by Exxon, which is a mixture of C<sub>11</sub>-C<sub>13</sub> isoparaffins.

5

Water

The compositions of the present invention comprise from about 50% to about 98.7%, more preferably from about 55% to about 85%, and most preferably from about 60% to about 75% of water.

**ADDITIONAL COMPONENTS**

10

Additional Surfactants

The compositions of the present invention can optionally comprise from about 0% to about 30%, preferably from about 2% to about 15%, and more preferably from about 4% to about 8% of a secondary surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof. Such surfactants are well-known to those skilled in the art. Preferably, these surfactants are deterative surfactants. By "deterative" is meant that these surfactants provide a cleansing or detergent benefit.

Nonlimiting examples of suitable secondary surfactants for use in the compositions of the present invention are disclosed in McCutcheon's, Detergents and Emulsifiers, North American edition (1986), published by Allured Publishing Corporation; McCutcheon's, Functional Materials, North American Edition (1992); U.S. Patent No. 5,151,210, to Steuri et al., issued September 29, 1992; U.S. Patent No. 5,151,209, to McCall et al., issued September 29, 1992; U.S. Patent No. 5,120,532, to Wells et al., issued June 9, 1992; U.S. Patent No. 5,011,681, to Ciotti et al., issued April 30, 1991; U.S. Patent No. 4,788,006, to Bolich, Jr. et al., issued November 29, 1988; U.S. Patent No. 4,741,855, to Grote et al, issued May 3, 1988; U.S. Patent No. 4,704,272, to Oh et al, issued November 3, 1987; U.S. Patent No. 4,557, 853, to Collins, issued December 10, 1985; U.S. Patent No. 4,421,769, to Dixon et al., issued December 20, 1983; and U.S. Patent No. 3,755,560, to Dickert et al., issued August 28, 1973; each of these documents being incorporated herein by reference in its entirety.

The following are nonlimiting examples of surfactants useful herein. It should be recognized that care must be taken in determining the level of these

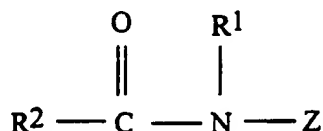
surfactant materials used so as not to interfere with the deposition and performance characteristics of the styling polymer. Also, care must be taken to select the additional surfactant and its level, such that the mildness properties of the compositions are not compromised.

5        Among the nonionic surfactants that are useful herein are those that can be broadly defined as condensation products of long chain alcohols, e.g. C8-30 alcohols, with sugar or starch polymers, i.e., glycosides. These compounds can be represented by the formula  $(S)_n-O-R$  wherein S is a sugar moiety such as glucose, fructose, mannose, and galactose; n is an integer of from about 1 to about 1000, and  
10       R is a C8-30 alkyl group. Examples of long chain alcohols from which the alkyl group can be derived include decyl alcohol, cetyl alcohol, stearyl alcohol, lauryl alcohol, myristyl alcohol, oleyl alcohol, and the like. Preferred examples of these surfactants include those wherein S is a glucose moiety, R is a C8-20 alkyl group, and n is an integer of from about 1 to about 9. Commercially available examples of  
15       these surfactants include decyl polyglucoside (available as APG 325 CS from Henkel) and lauryl polyglucoside (available as APG 600CS and 625CS from Henkel).

Other useful nonionic surfactants include the condensation products of alkylene oxides with fatty acids (i.e. alkylene oxide esters of fatty acids). When  
20       these particular nonionics are used, it is preferable to use them at low concentrations, preferably in combination with one or more of the other surfactants disclosed herein. These materials have the general formula  $RCO(X)_nOH$  wherein R is a C10-30 alkyl group, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (i.e. derived from propylene glycol or oxide), and n is an  
25       integer from about 1 to about 100. Other nonionic surfactants are the condensation products of alkylene oxides with 2 moles of fatty acids (i.e. alkylene oxide diesters of fatty acids). These materials have the general formula  $RCO(X)_nOOCR$  wherein R is a C10-30 alkyl group, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (i.e. derived from propylene glycol or oxide), and n is an  
30       integer from about 1 to about 100. Other nonionic surfactants are the condensation products of alkylene oxides with fatty alcohols (i.e. alkylene oxide ethers of fatty alcohols). These materials have the general formula  $R(X)_nOR'$  wherein R is a C10-30 alkyl group, X is  $-OCH_2CH_2-$  (i.e. derived from ethylene glycol or oxide) or  $-OCH_2CHCH_3-$  (i.e. derived from propylene glycol or oxide), and n is an integer  
35       from about 1 to about 100 and R' is H or a C10-30 alkyl group. Still other nonionic surfactants are the condensation products of alkylene oxides with both fatty acids and fatty alcohols [i.e. wherein the polyalkylene oxide portion is esterified on one

end with a fatty acid and etherified (i.e. connected via an ether linkage) on the other end with a fatty alcohol]. These materials have the general formula  $\text{RCO}(\text{X})_n\text{OR}'$  wherein R and R' are C10-30 alkyl groups, X is  $-\text{OCH}_2\text{CH}_2-$  (i.e. derived from ethylene glycol or oxide) or  $-\text{OCH}_2\text{CHCH}_3-$  (derived from propylene glycol or oxide), and n is an integer from about 1 to about 100. Nonlimiting examples of these alkylene oxide derived nonionic surfactants include ceteth-1, ceteth-2, ceteth-6, ceteth-10, ceteth-12, cetareth-2, cetareth-6, cetareth-10, cetareth-12, steareth-1, steareth-2, steareth-6, steareth-10, steareth-12, PEG-2 stearate, PEG-4 stearate, PEG-6 stearate, PEG-10 stearate, PEG-12 stearate, PEG-20 glyceryl stearate, PEG-80 glyceryl tallowate, PPG-10 glyceryl stearate, PEG-30 glyceryl cocoate, PEG-80 glyceryl cocoate, PEG-200 glyceryl tallowate, PEG-8 dilaurate, PEG-10 distearate, and mixtures thereof.

Still other useful nonionic surfactants include polyhydroxy fatty acid amide surfactants corresponding to the structural formula:



wherein:  $\text{R}^1$  is H,  $\text{C}_1\text{-C}_4$  alkyl, 2-hydroxyethyl, 2-hydroxy-propyl, preferably  $\text{C}_1\text{-C}_4$  alkyl, more preferably methyl or ethyl, most preferably methyl;  $\text{R}^2$  is  $\text{C}_5\text{-C}_{31}$  alkyl or alkenyl, preferably  $\text{C}_7\text{-C}_{19}$  alkyl or alkenyl, more preferably  $\text{C}_9\text{-C}_{17}$  alkyl or alkenyl, most preferably  $\text{C}_{11}\text{-C}_{15}$  alkyl or alkenyl; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with a least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably is a sugar moiety selected from the group consisting of glucose, fructose, maltose, lactose, galactose, mannose, xylose, and mixtures thereof. An especially preferred surfactant corresponding to the above structure is coconut alkyl N-methyl glucoside amide (i.e., wherein the  $\text{R}^2\text{CO}-$  moiety is derived from coconut oil fatty acids). Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd.; U.S. Patent No. 2,965,576, to E.R. Wilson, issued December 20, 1960; U.S. Patent No. 2,703,798, to A.M. Schwartz, issued March 8, 1955; and U.S. Patent No. 1,985,424, to Piggott, issued December 25, 1934; which are incorporated herein by reference in their entirety.



A wide variety of anionic surfactants are useful herein. See, e.g., U.S. Patent No. 3,929,678, to Laughlin et al., issued December 30, 1975, which is incorporated herein by reference in its entirety. Nonlimiting examples of anionic surfactants include the alkoyl isethionates, and the alkyl and alkyl ether sulfates. The alkoyl isethionates typically have the formula  $\text{RCO-OCH}_2\text{CH}_2\text{SO}_3\text{M}$  wherein R is alkyl or alkenyl of from about 10 to about 30 carbon atoms, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Nonlimiting examples of these isethionates include those alkoyl isethionates selected from the group consisting of ammonium cocoyl isethionate, sodium cocoyl isethionate, sodium lauroyl isethionate, sodium stearyl isethionate, and mixtures thereof.

The alkyl and alkyl ether sulfates typically have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 10 to about 30 carbon atoms, x is from about 1 to about 10, and M is a water-soluble cation such as ammonium, sodium, potassium and triethanolamine. Examples of these materials are sodium lauryl sulfate and ammonium lauryl sulfate.

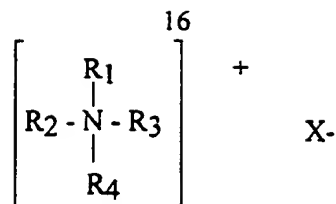
Another suitable class of anionic surfactants are the water-soluble salts of the organic, sulfuric acid reaction products of the general formula:



wherein  $\text{R}_1$  is chosen from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 16, carbon atoms; and M is a cation. Still other anionic synthetic surfactants include the class designated as succinamates, olefin sulfonates having about 12 to about 24 carbon atoms, and b-alkyloxy alkane sulfonates.

Other anionic materials useful herein are soaps (i.e. alkali metal salts, e.g., sodium or potassium salts) of fatty acids, typically having from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms. The fatty acids used in making the soaps can be obtained from natural sources such as, for instance, plant or animal-derived glycerides (e.g., palm oil, coconut oil, soybean oil, castor oil, tallow, lard, etc.) The fatty acids can also be synthetically prepared. Soaps are described in more detail in U.S. Patent No. 4,557,853, cited above.

Cationic surfactants can also be utilized in the present invention. Nonlimiting examples of cationic surfactants useful herein include cationic ammonium salts such as those having the formula:



wherein  $\text{R}_1$  is selected from an alkyl group having from about 12 to about 22 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 22 carbon atoms;  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are independently selected from hydrogen, an alkyl group having from about 1 to about 22 carbon atoms, or aromatic, aryl or alkaryl groups having from about 12 to about 22 carbon atoms; and X is an anion selected from chloride, bromide, iodide, acetate, phosphate, nitrate, sulfate, methyl sulfate, ethyl sulfate, tosylate, lactate, citrate, glycolate, and mixtures thereof. Additionally, the alkyl groups can also contain ether linkages, or hydroxy or amino group substituents (e.g., the alkyl groups can contain polyethylene glycol and polypropylene glycol moieties).

More preferably,  $\text{R}_1$  is an alkyl group having from about 12 to about 22 carbon atoms;  $\text{R}_2$  is selected from H or an alkyl group having from about 1 to about 22 carbon atoms;  $\text{R}_3$  and  $\text{R}_4$  are independently selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and X is as described in the previous paragraph.

Most preferably,  $\text{R}_1$  is an alkyl group having from about 12 to about 22 carbon atoms;  $\text{R}_2$ ,  $\text{R}_3$ , and  $\text{R}_4$  are selected from H or an alkyl group having from about 1 to about 3 carbon atoms; and X is as described previously.

Other ammonium quaternary and amino surfactants include those in the form of ring structures formed by covalently linking of the radicals. Examples of such cationic surfactants include imidazolines, imidazoliniums, and pyridiniums, etc., wherein said surfactant has at least one nonionic hydrophile-containing radical as set forth above. Specific examples include 2-heptadecyl-4,5-dihydro-1H-imidazol-1-ethanol, 4,5-dihydro-1-(2-hydroxyethyl)-2-isoheptadecyl-1-phenylmethylimidazolium chloride, and 1-[2-oxo-2-[[2-[(1-oxooctadecyl)oxy]ethyl]amino]ethyl] pyridinium chloride.

Alternatively, other useful cationic surfactants include amino-amides, wherein in the above structure  $\text{R}_1$  is alternatively  $\text{R}_5\text{CO}-(\text{CH}_2)_n-$ , wherein  $\text{R}_5$  is an alkyl group having from about 12 to about 22 carbon atoms, and  $n$  is an integer from about 2 to about 6, more preferably from about 2 to about 4, and most preferably from about 2 to about 3. Nonlimiting examples of these cationic emulsifiers include stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate)

ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Nonlimiting examples of quaternary ammonium salt cationic surfactants include those selected from the group consisting of cetyl ammonium chloride, cetyl ammonium bromide, lauryl ammonium chloride, lauryl ammonium bromide, stearyl ammonium chloride, stearyl ammonium bromide, cetyl dimethyl ammonium chloride, cetyl dimethyl ammonium bromide, lauryl dimethyl ammonium chloride, lauryl dimethyl ammonium bromide, stearyl dimethyl ammonium chloride, stearyl dimethyl ammonium bromide, cetyl trimethyl ammonium chloride, cetyl trimethyl ammonium bromide, lauryl trimethyl ammonium chloride, lauryl trimethyl ammonium bromide, stearyl trimethyl ammonium chloride, stearyl trimethyl ammonium bromide, lauryl dimethyl ammonium chloride, stearyl dimethyl cetyl ditallow dimethyl ammonium chloride, dicetyl ammonium chloride, dicetyl ammonium bromide, dilauryl ammonium chloride, dilauryl ammonium bromide, distearyl ammonium chloride, distearyl ammonium bromide, dicetyl methyl ammonium chloride, dicetyl methyl ammonium bromide, dilauryl methyl ammonium chloride, dilauryl methyl ammonium bromide, distearyl methyl ammonium chloride, distearyl dimethyl ammonium chloride, distearyl methyl ammonium bromide, and mixtures thereof. Additional quaternary ammonium salts include those wherein the C12 to C22 alkyl carbon chain is derived from a tallow fatty acid or from a coconut fatty acid. The term "tallow" refers to an alkyl group derived from tallow fatty acids (usually hydrogenated tallow fatty acids), which generally have mixtures of alkyl chains in the C16 to C18 range. The term "coconut" refers to an alkyl group derived from a coconut fatty acid, which generally have mixtures of alkyl chains in the C12 to C14 range. Examples of quaternary ammonium salts derived from these tallow and coconut sources include ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated tallow) dimethyl ammonium chloride, di(hydrogenated tallow) dimethyl ammonium acetate, ditallow dipropyl ammonium phosphate, ditallow dimethyl ammonium nitrate, di(coconutalkyl)dimethyl ammonium chloride, di(coconutalkyl)dimethyl ammonium bromide, tallow ammonium chloride, coconut ammonium chloride, stearamidopropyl PG-dimonium chloride phosphate, stearamidopropyl ethyldimonium ethosulfate, stearamidopropyl dimethyl (myristyl acetate) ammonium chloride, stearamidopropyl dimethyl cetearyl ammonium tosylate, stearamidopropyl dimethyl ammonium chloride, stearamidopropyl dimethyl ammonium lactate, and mixtures thereof.

Other cationic surfactants for use in the present invention are those which are useful for providing conditioning benefits, particularly hair conditioning properties and which are quaternary ammonium or amino compounds having at least one N-radical containing one or more nonionic hydrophilic moieties selected from alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, and alkylester moieties, and combinations thereof. The surfactant contains at least one hydrophilic moiety within 4 (inclusive), preferably within 3 (inclusive), carbon atoms of the quaternary nitrogen or cationic amino nitrogen. For purposes herein, this means that the closest non-carbon atom in the hydrophilic moiety to the cationic nitrogen must be within the stated number of carbon atoms relative to said nitrogen. Additionally, carbon atoms that are part of a hydrophilic moiety, e.g., carbon atoms in a hydrophilic polyoxyalkylene (e.g., -CH<sub>2</sub>-CH<sub>2</sub>-O-), that are adjacent to other hydrophilic moieties are not counted as when determining the number of hydrophilic moieties within 4, or preferably 3, carbon atoms of the cationic nitrogen. In general, the alkyl portion of any hydrophilic moiety is preferably a C<sub>1</sub>-C<sub>3</sub> alkyl. Suitable hydrophile-containing radicals include, for example, ethoxy, propoxy, polyoxyethylene, polyoxypropylene, ethylamido, propylamido, hydroxymethyl, hydroxyethyl, hydroxypropyl, methylester, ethylester, propylester, or mixtures thereof, as nonionic hydrophile moieties.

Specific examples of preferred quaternary ammonium salts include polyoxyethylene (2) stearyl methyl ammonium chloride, methyl bis (hydrogenated tallowamidoethyl) 2-hydroxyethyl ammonium methyl sulfate, polyoxypropylene (9) diethyl methyl ammonium chloride, tripolyoxyethylene (total PEG=10) stearyl ammonium phosphate, bis(N-hydroxyethyl -2-oleyl imidazolium chloride) polyethylene glycol (12), and isododecylbenzyl triethanolammonium chloride.

Salts of primary, secondary and tertiary fatty amines are also preferred cationic surfactant materials. The alkyl groups of such amines preferably have from about 1 to about 30 carbon atoms and must contain at least one, preferably 2 to about 10, nonionic hydrophilic moieties selected from alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, and alkylester moieties, and mixtures thereof. Secondary and tertiary amines are preferred, tertiary amines are particularly preferred. Specific examples of suitable amines include diethyl aminoethyl polyoxyethylene (5) laurate, coco-polyglyceryl-4 hydroxypropyl dihydroxy ethylamine, and dihydroxyethyl tallowamine hydrochloride.

The cationic conditioning agents for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

Examples of amphoteric and zwitterionic surfactants which can be used in the compositions of the present invention are those which are broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 22 carbon atoms (preferably C<sub>8</sub> - C<sub>18</sub>) and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. Examples are alkyl imino acetates, and iminodialkanoates and aminoalkanoates of the formulas  $RN(CH_2)_mCO_2M]_2$  and  $RNH(CH_2)_mCO_2M$  wherein m is from 1 to 4, R is a C<sub>8</sub>-C<sub>22</sub> alkyl or alkenyl, and M is H, alkali metal, alkaline earth metal ammonium, or alkanolammonium. Also included are imidazolinium and ammonium derivatives. Specific examples of suitable amphoteric surfactants include sodium 3-dodecyl-aminopropionate, sodium 3-dodecylaminopropane sulfonate, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 2,658,072 which is incorporated herein by reference in its entirety; N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091 which is incorporated herein by reference in its entirety; and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378, which is incorporated herein by reference in its entirety. Other examples of useful amphoterics include phosphates, such as coamidopropyl PG-dimonium chloride phosphate (commercially available as Monaquat PTC, from Mona Corp.).

Also useful herein as amphoteric or zwitterionic surfactants are the betaines. Examples of betaines include the higher alkyl betaines, such as coco dimethyl carboxymethyl betaine, lauryl dimethyl carboxymethyl betaine, lauryl dimethyl alphacarboxyethyl betaine, cetyl dimethyl carboxymethyl betaine, cetyl dimethyl betaine (available as Lonzaïne 16SP from Lonza Corp.), lauryl bis-(2-hydroxyethyl) carboxymethyl betaine, stearyl bis-(2-hydroxypropyl) carboxymethyl betaine, oleyl dimethyl gamma-carboxypropyl betaine, lauryl bis-(2-hydroxypropyl)alpha-carboxyethyl betaine, coco dimethyl sulfopropyl betaine, stearyl dimethyl sulfopropyl betaine, lauryl dimethyl sulfoethyl betaine, lauryl bis-(2-hydroxyethyl) sulfopropyl betaine, and amidobetaines and amidosulfobetaines (wherein the  $RCONH(CH_2)_3$  radical is attached to the nitrogen atom of the betaine), oleyl betaine (available as amphoteric Velvetex OLB-50 from Henkel), and cocamidopropyl betaine (available as Velvetex BK-35 and BA-35 from Henkel).

Other useful amphoteric and zwitterionic surfactants include the sultaines and hydroxysultaines such as cocamidopropyl hydroxysultaine (available as Mirataïne CBS from Rhone-Poulenc), and the alkanoyl sarcosinates corresponding to the

formula  $\text{RCON}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CO}_2\text{M}$  wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, and M is a water-soluble cation such as ammonium, sodium, potassium and trialkanolamine (e.g., triethanolamine).

The above-mentioned surfactants can optionally be used in combination with  
5 AGS in the hair care compositions of the present invention. Preferred surfactants for use in the present shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth  
10 sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine  
15 lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, cocoamidopropyl betaine, cocobetaine, lauryl amido propyl betaine, oleyl betaine, and cocoamphocarboxyglycinate.

The most preferred of the optional surfactants for use herein are ammonium  
20 laureth sulfate and cocoamidopropyl betaine.

#### Conditioning Agent

The shampoo compositions of the present invention also preferably comprise a hair conditioning agent. It is this agent that provides additional hair conditioning benefits such as ease of combing, soft hair feel, and manageability to the user. The resulting  
25 shampoo composition provides hair cleaning, styling and conditioning benefits in one product.

Cationic surfactants, as described above, can be used to give some conditioning benefits in the present compositions. Similarly protein derivatives, such as hydrolyzed animal proteins, for example, Crotein SPA (Croda) or Lexeine X250 (Inolex) or Poly-  
30 peptide LSN (Stephan), can be used to provide conditioning benefits.

The hair conditioning agent of the present invention can be a non-volatile siloxane or a siloxane-containing material and is present at a level of from about 0.01% to about 10% of the shampoo composition, preferably from about 0.1% to about 5%, most preferably from about 0.2% to about 3%.

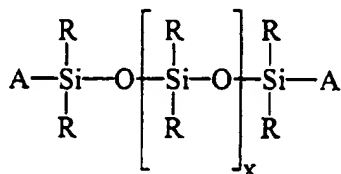
35 Siloxanes (see, for example, U.S. Patent 3,208,911, Oppliger, issued September 28, 1965) and siloxane-containing polymers have been taught for use in hair conditioning compositions. U.S. Patent 4,601,902, Fridd et al., issued July 22, 1986, describes hair

conditioning or shampoo/conditioner compositions which include a polydiorganosiloxane having quaternary ammonium substituted groups attached to the silicon, and a polydiorganosiloxane having silicon-bonded substituents which are amino-substituted hydrocarbon groups. U.S. Patent 4,654,161, Kollmeier et al., issued March 31, 1987, describes a group of organopolysiloxanes containing betaine substituents. When used in hair care compositions, these compounds are said to provide good conditioning, compatibility with anionic components, hair substantivity, and low skin irritation. U.S. Patent 4,563,347, Starch, issued January 7, 1986, relates to hair conditioning compositions which include siloxane components containing substituents to provide attachment to hair. Japanese Published Application 56-129,300, Lion Corporation, published October 9, 1981, relates to shampoo conditioner compositions which include an organopolysiloxane-oxyalkylene copolymer together with an acrylic resin. U.S. Patent 4,479,893, Hirota et al., issued October 30, 1984, describes shampoo conditioner compositions containing a phosphate ester surfactant and a silicon derivative (e.g., polyether- or alcohol-modified siloxanes). Polyether-modified polysiloxanes are also disclosed for use in shampoos in U.S. Patent 3,957,970, Korkis, issued May 18, 1976. U.S. Patent 4,185,087, Morlino, issued January 22, 1980, describes quaternary nitrogen derivatives of trialkylamino hydroxy organosilicon compounds which are said to have superior hair conditioning properties. Each of the above mentioned documents in this paragraph are incorporated herein by reference in its entirety.

Siloxane-derived materials have also been used in hair styling compositions. Japanese Published Application 56-092,811, Lion Corporation, published December 27, 1979, describes hair setting compositions which comprise an amphoteric acrylic resin, a polyoxyalkylene-denatured organopolysiloxane, and polyethylene glycol. U.S. Patent 4,744,978, Homan et al., issued May 17, 1988, describes hair styling compositions (such as hair sprays) which include the combination of a carboxyfunctional polydimethylsiloxane and a cationic organic polymer containing amine or ammonium groups. Hair styling compositions which include polydiorganosiloxanes and a cationic organic polymer are taught in U.S. Patent 4,733,677, Gee et al., issued March 29, 1988, and U.S. Patent 4,724,851, Cornwall et al., issued February 16, 1988. Finally, European Patent Application 117,360, Cantrell et al., published September 5, 1984, discloses compositions, containing a siloxane polymer having at least one nitrogen-hydrogen bond, a surfactant, and a solubilized titanate, zirconate or germanate, which act as both a conditioner and a hair styling aid. Each of the above mentioned documents in this paragraph are incorporated herein by reference in its entirety.

Nonvolatile silicone fluids are useful as the conditioning agent component in the shampoo compositions of the present invention. Examples of such materials include

polydimethylsiloxane gums, aminosilicones and phenylsilicones. More specifically, materials such as polyalkyl or polyaryl siloxanes with the following structure:



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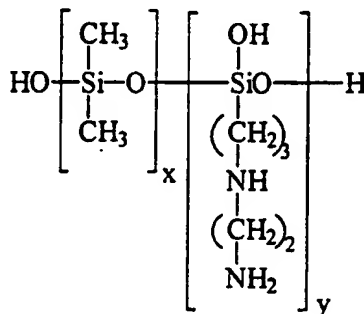
wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000 may be used. A represents groups which block the ends of the silicone chains.

The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) may have any structure as long as the resulting silicones remain fluid at room temperature, are hydrophobic, are neither irritating, toxic nor otherwise harmful when applied to the hair, are compatible with the other components of the composition, are chemically stable under normal use and storage conditions, and are capable of being deposited on the hair.

Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicone atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

Suitable methods for preparing these silicone materials are disclosed in U.S. Patents 2,826,551 and 3,964,500 and references cited therein, each of which are incorporated by reference in its entirety. Silicones useful in the present invention are also commercially available. Suitable examples include Viscasil, a trademark of the General Electric Company and silicones offered by Dow Corning Corporation and by SWS Silicones, a division of Stauffer Chemical Company.

Other-useful silicone conditioning materials include materials of the formula:





in which x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

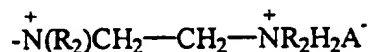
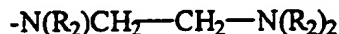
Other silicone cationic polymer conditioning agents which can be used in the present compositions correspond to the formula:



in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sup>1</sup>-C<sup>8</sup> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0;

b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10;

R<sup>1</sup> is a monovalent radical of formula C<sub>q</sub>H<sup>2</sup><sub>q</sub>L in which q is an integer from 2 to 8 and L is chosen from the groups

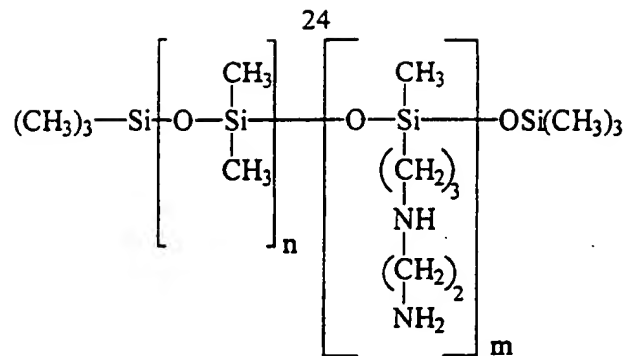


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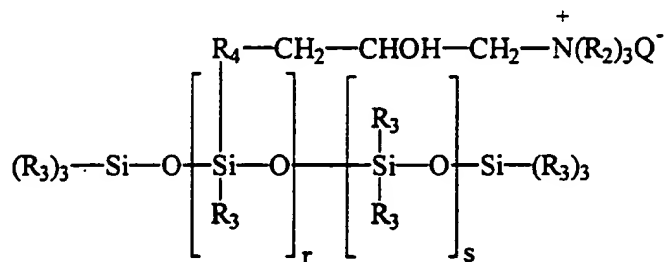
in which R<sub>2</sub> is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A<sup>-</sup> denotes a halide ion.

These compounds are described in greater detail in European Patent Application EP 95,238, which is incorporated by reference herein in its entirety. An especially preferred polymer corresponding to this formula is the polymer known as "trimethylsilylamodimethicone" of formula:

25



Other silicone cationic polymer conditioning agents which can be used in the present compositions correspond to the formula:



in which R<sub>3</sub> denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, and more especially an alkyl or alkenyl radical such as methyl;

R<sub>4</sub> denotes a hydrocarbon radical such as, preferably a C<sub>1</sub>-C<sub>18</sub> alkylene radical or a C<sub>1</sub>-C<sub>18</sub>, and preferably C<sub>1</sub>-C<sub>8</sub>, alkyleneoxy radical;

Q is a halide ion, preferably chloride;

r denotes an average statistical value from 2 to 20, preferably from 2 to 8;

s denotes an average statistical value from 20 to 200, and preferably from 20 to 50.

These compounds are described in greater detail in U.S. Patent 4,185,017, which is incorporated by reference in its entirety. A polymer of this class which is especially preferred is that sold by UNION CARBIDE under the name "UCAR SILICONE ALE 56".

The compositions of the present invention can also comprise a water soluble, cationic hair conditioning agent. Although these cationic hair conditioning agents are not necessary for the styling benefit, they have been shown to aid deposition of the hair styling polymer and achievement of the styling benefit. The cationic hair conditioning agent hereof will generally be present at levels of from about 0.05% to about 5%, preferably from about 0.1% to about 4%, more preferably from about 0.2% to about 3%, by weight, of the shampoo composition. The water soluble

cationic conditioning agents hereof can include organic cationic polymers, organic cationic surfactants, and cationic silicone fluids. By "water soluble", what is meant is a material which is soluble in water at a concentration of 0.1% in water (distilled or equivalent) at 25°C. Preferably, the water soluble cationic conditioning agent  
5 will be soluble at 0.5% concentration, more preferably at 1.0% concentration. In general, the polymer will be considered soluble if it forms a substantially clear solution to the naked eye.

The water-soluble cationic polymers useful in the hair conditioning agent hereof are polymers that can provide conditioning benefits to hair and that are  
10 soluble in the shampoo composition. Any cationic polymers which can provide these benefits can be used. As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers.

The cationic organic polymers hereof will generally have a weight average  
15 molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, or a mixture thereof.

Those skilled in the art will recognize that the charge density of  
20 amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The polymer should be within the above solubility limits at the pH of intended use, which will in general be from about pH 3 to about pH 9, most generally from about pH 4 to about pH 8.

Any anionic counterions can be utilized for the cationic polymers so long as  
25 the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a  
30 substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient  
35 Dictionary, 5th edition, edited by Wenninger and McEwen, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1993).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C<sub>1</sub>-C<sub>7</sub> alkyl groups, more preferably C<sub>1</sub>-C<sub>3</sub> alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the shampoo. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C<sub>1</sub>-C<sub>7</sub> alkyl, more preferably a C<sub>1</sub>-C<sub>3</sub> alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are C<sub>1</sub>-C<sub>7</sub> alkyls, preferably lower alkyls such as the C<sub>1</sub>-C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls.

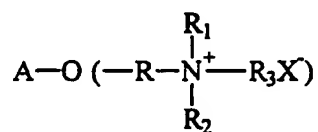
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT trade-

name (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N);  
 5 cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having  
 10 from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include  
 15 those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose  
 20 anhydroglucose residual,

R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof,

R1, R2, and R3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon  
 25 atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R1, R2 and R3) preferably being about 20 or less, and

X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose  
 30 reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted opoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison,  
 35 NJ, USA) under the tradename Polymer LM-200.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein).

As discussed above, the cationic polymer hereof is water soluble. This does not mean, however, that it must be soluble in the shampoo composition. Preferably however, the cationic polymer is either soluble in the shampoo composition, or in a coacervate phase in the shampoo composition formed by the cationic polymer and anionic material. Coacervates of the cationic polymer can be formed with anionic surfactants or with anionic polymers that can optionally be added to the compositions hereof (e.g., sodium polystyrene sulfonate).

Coacervate formation is dependent upon a variety of criteria such as molecular weight, concentration, and ratio of interacting ionic materials, ionic strength (including modification of ionic strength, for example, by addition of salts), charge density of the cationic and anionic species, pH, and temperature. Coacervate systems and the effect of these parameters has previously been studied. See, for example, J. Caelles, et al., "Anionic and Cationic Compounds in Mixed Systems", *Cosmetics & Toiletries*, Vol. 106, April 1991, pp 49-54, C. J. van Oss, "Coacervation, Complex-Coacervation and Flocculation", *J. Dispersion Science and Technology*, Vol. 9 (5,6), 1988-89, pp 561-573, and D. J. Burgess, "Practical Analysis of Complex Coacervate Systems", *J. of Colloid and Interface Science*, Vol. 140, No. 1, November 1990, pp 227-238.

It is believed to be particularly advantageous for the cationic polymer to be present in the shampoo in a coacervate phase, or to form a coacervate phase upon application or rinsing of the shampoo to or from the hair. Coacervates are believed to more readily deposit on the hair. Thus, in general, it is preferred that the cationic polymer exist in the shampoo as a coacervate phase or form a coacervate phase upon dilution. If not already a coacervate in the shampoo, the cationic polymer will preferably exist in a coacervate form in the shampoo upon dilution with water to a water:shampoo composition weight ratio of about 20:1, more preferably at about 10:1, even more preferably at about 8:1.

Techniques for analysis of formation of coacervates are known in the art. For example, microscopic analyses of the shampoo compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the

composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the composition.

Conditioning ingredients such as oils and emollients can also be incorporated into the styling shampoo compositions of this invention.

5

#### Other Optional Ingredients

The high lather styling shampoo compositions herein can contain a variety of other optional components suitable for rendering such compositions more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such conventional optional ingredients are well-known to those skilled in the art, e.g., pearlescent aids, such as coated mica, ethylene glycol distearate, and PEG 3 distearate; opacifiers such as  $\text{TiO}_2$ ; preservatives, such as benzyl alcohol, Glydant, Kathon, methyl paraben, propyl paraben and imidazolidinyl urea; fatty alcohols, such as cetearyl alcohol; sodium chloride; sodium sulfate; polyvinyl alcohol; ethyl alcohol; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, monosodium phosphate, disodium phosphate, sodium hydroxide, and sodium carbonate; coloring agents, such as any of the FD&C or D&C dyes; perfumes; sequestering agents, such as disodium ethylenediamine tetra-acetate; and polymer plasticizing agents, such as glycerin and propylene glycol. The present compositions can also optionally comprise thickeners and viscosity modifiers, such as a diethanolamide of a long chain fatty acid (e.g., PEG 3 lauric diethanolamide), lauramide DEA, cocomonooethanol amide, guar gum, xanthan gum, Crothix (PEG 150 Pentaerythrityl Tetrastearate), methyl cellulose, hydroxyethyl cellulose, starches and starch derivatives. Various salts and electrolytes, preferably sodium chloride, can also be used as needed to adjust the viscosity of the present compositions. The compositions can comprise a nonionic long chain alkylated cellulose ether thickener such as those materials described in U.S. Patent 4,228,277, Landoll, issued October 14, 1980, which is incorporated herein by reference in its entirety.

Such optional ingredients generally are used individually at levels of from about 0.01% to about 10.0%, preferably from about 0.05% to about 5.0%, of the shampoo composition.

As with all compositions, the present invention should not contain optional components which unduly interfere with the cleaning and hair style holding performance of the present shampoo compositions.

35

#### Method of Making

The styling shampoo compositions of the present invention can be made using conventional formulation and mixing techniques. The hair styling polymer should

first be dissolved in the non-polar volatile solvent. The remaining ingredients are combined in a separate vessel and the polymer and solvent mixture is added to these remaining ingredients. The composition should have a final viscosity of from about 1500 to about 12,000 cps. The viscosity of the composition can be adjusted using sodium chloride as needed.

#### Method of Use

The high lather styling shampoo compositions of the present invention are used in conventional ways to provide cleansing and styling hold benefits. Such methods generally involve application of an effective amount of the shampoo product to the wet hair, which is massaged through and then rinsed from the hair. By "effective amount" is meant an amount sufficient to provide the hair cleaning and styling hold benefits desired considering the length and texture of the hair. After the hair is shampooed with the compositions of the present invention, the hair is dried and styled in the usual ways of the user, e.g. combing, brushing, blow drying, curling, heat drying, etc.

#### EXAMPLES

The following examples illustrate the present invention. It will be appreciated that other modifications of the present invention within the skill of those in the cosmetic composition formulation art can be undertaken without departing from the spirit and scope of this invention.

Ingredients are identified by chemical or CTFA name.

All parts, percentages, and ratios herein are by weight unless otherwise specified.

#### EXAMPLES A-E

The following table defines the hair styling agents of the present invention. These hair styling agents are mixtures of hair styling polymers and non-polar volatile solvents which are used in Examples I-IX. All ratios herein are given on a weight/weight basis. It should be noted that the numbers in parentheses following the polymers indicates the relative weight ratios of the monomers.

		w/w ratio
30	<b>Mixture A.</b>	
	Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (90/10w/w)	40
	Solvent: isododecane	60
	<b>Mixture B.</b>	
	Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (90/10w/w)	50
	Solvent: isododecane	50
	<b>Mixture C.</b>	
	Polymer: t-butyl methacrylate/2-ethylhexyl methacrylate (50/50w/w)	40



Solvent: isohexadecane	60
<b>Mixture D.</b>	
Polymer: t-butyl methacrylate/2-ethylhexyl methacrylate (50/50w/w)	30
Solvent: Isoparaffin Blend (C <sub>11</sub> -C <sub>12</sub> ) <sup>1</sup>	70
<b>Mixture E.</b>	
Polymer: t-butyl acrylate/2-ethylhexyl methacrylate (60/40w/w)	40
Solvent: Isoparaffin Blend (C <sub>11</sub> -C <sub>13</sub> ) <sup>2</sup>	60

<sup>1</sup> Sold as Isopar H by Exxon, which is a mixture of C11-C12 isoparaffins.

<sup>2</sup> Sold as Isopar L by Exxon, which is a mixture of C11-C13 isoparaffins.

- 5 The hair styling polymer and non-polar volatile solvent mixture is prepared by placing the appropriate hair styling polymer into a suitable vessel, and adding the appropriate non-polar volatile solvent to the vessel. The mixture is then stirred while heating to about 160°-180° F until the polymer is completely dissolved.

#### EXAMPLES I-V

- 10 The following hair shampoo compositions are representative of the present invention.

<u>Component</u>	<u>Weight %</u>				
	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>
Ammonium Laureth Sulfate	2.00	2.00	2.00	8.00	2.00
Cocoamidopropyl Betaine F	6.00	6.00	6.00	6.00	6.00
Ammonium Lauryl Sulfate	0.00	2.00	0.00	0.00	0.00
Alkyl Glycerol Sulfonate	10.00	8.00	10.00	4.00	10.00
Mixture A	6.00	---	---	---	---
Mixture B	---	8.00	---	---	---
Mixture C	---	---	4.00	---	---
Mixture D	---	---	---	4.00	---
Mixture E	---	---	---	---	8.00
Monosodium Phosphate	0.1	0.1	0.1	0.1	0.1
Disodium Phosphate	0.2	0.2	0.2	0.2	0.2
Glycol Distearate	2.00	2.00	2.00	2.00	2.00
Cocomonoethanol amide	0.70	0.70	0.70	0.70	0.70
Fragrance	0.8	0.8	0.8	0.8	0.8
PEG-150 Pentaerythrityl					
Tetrastearate	0.40	0.45	0.15	0.30	0.45
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18	0.18	0.18
Polyquaternium 10	0.30	0.50	0.40	0.30	0.50
Dimethicone <sup>1</sup>	0.00	0.00	0.00	1.50	1.50
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Water	QS 100	QS 100	QS 100	QS 100	QS 100

1 This material is a 40/60 weight ratio blend of polydimethylsiloxane gum (GE SE 76, available from General Electric Company, Silicone Products Division, Waterford, NY, USA) and polydimethylsiloxane fluid (about 350 centistokes).

5 In a suitable vessel, the glycol distearate, cocomonoeethanol amide, PEG-150 pentaerythrityl tetrastearate, cetyl alcohol, stearyl alcohol, monosodium phosphate, and disodium phosphate are combined with all of the AGS and half of each of the remaining surfactants [ammonium laureth sulfate, cocoamidopropyl Betaine F, (and ammonium lauryl sulfate when present)]. The mixture is then heated to about 160-180°F and stirred until the solids are melted. This mixture is cooled to room  
10 temperature. In another vessel, the polyquaternium-10 is predissolved in the water, then added to the other cooled ingredients with mixing. The appropriate polymer mixture and the remaining ingredients are added with stirring. The resulting shampoo product is useful for both cleansing the hair and for providing hair style holding benefits.

15

#### EXAMPLE VI

The following hair shampoo composition is representative of the present invention.

<u>Component</u>	<u>Weight %</u>
Alkyl Glycerol Sulfonate	14.00
Mixture A	6.00
Monosodium Phosphate	0.1
Disodium Phosphate	0.2
Glycol Distearate	2.00
Cocomonoethanol amide	0.70
Fragrance	0.8
PEG-150 Pentaerythrityl	
Tetrastearate	0.40
Cetyl Alcohol	0.42
Stearyl Alcohol	0.18
Polyquaternium 10	0.30
DMDM Hydantoin	0.37
Water	QS

20 This products is prepared using the method described in Example I-V.

This shampoo product is useful for both cleansing the hair and for providing hair style holding benefits.

#### EXAMPLES VII-IX

25 The following are hair shampoo compositions which are representative of the present invention.

<u>Component</u>	<u>Weight %</u>		
	VII	VIII	IX
Ammonium Laureth Sulfate	2.00	2.00	2.00
Cocoamidopropyl Betaine F	6.00	6.00	6.00
Ammonium Lauryl Sulfate	0.00	0.00	0.00
Alkyl Glycerol Sulfonate	10.00	10.00	10.00
Mixture A	9.00	3.0	1.50
Monosodium Phosphate	0.1	0.1	0.1
Disodium Phosphate	0.2	0.2	0.2
Glycol Distearate	2.00	2.00	2.00
Cocomonoethanol amide	0.70	0.70	0.70
Fragrance	0.8	0.8	0.8
PEG-150 Pentaerythrityl			
Tetrastearate	0.50	0.15	---
Cetyl Alcohol	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18
Polyquaternium 10	0.50	0.30	0.30
Dimethicone <sup>1</sup>	0.00	0.00	0.00
DMDM Hydantoin	0.37	0.37	0.37
Water	QS 100	QS 100	QS 100

1 This material is a 40/60 weight ratio blend of polydimethylsiloxane gum (GE SE 76, available from General Electric Company, Silicone Products Division, Waterford, NY, USA) and polydimethylsiloxane fluid (about 350 centistokes).

5 These products are prepared using the method described in Example I-V.

These shampoo products are useful for both cleansing the hair and for providing hair style holding benefits.

## WHAT IS CLAIMED IS:

1. A lathering, hair styling shampoo composition comprising:
  - (a) from 2% to 25%, by weight, of an alkyl glyceryl ether sulfonate surfactant;
  - (b) from 0.1% to 10%, by weight, of a hair styling polymer;
  - (c) from 0.1% to 10%, by weight, of a non-polar volatile solvent for solubilizing said hair styling polymer, said hair styling polymer having a boiling point of less than or equal to 300°C., and a solubility in water at 25°C of less than 0.2% by weight; and
  - (d) from 50% to 97.8% water;wherein the weight ratio of said hair styling polymer to said non-polar volatile solvent is from 10:90 to 70:30.
2. The shampoo composition of Claim 1 wherein the ratio of said hair styling polymer to said non-polar volatile solvent is from 30:70 to 60:40 and wherein said non-polar volatile solvent has a boiling point from 90 °C to 260 °C.
3. The shampoo composition of any preceding Claim comprising from 0.5% to 5% of said non-polar volatile solvent, preferably wherein said non-polar volatile solvent is selected from the group consisting of hydrocarbons, ethers, and mixtures thereof, more preferably a hydrocarbon.
4. The shampoo composition of any preceding C wherein said hydrocarbon is a straight or branched chain hydrocarbon having from 8 to 18 carbon atoms, preferably selected from the group consisting of dodecane, isododecane, isotetradecane, isohexadecane, 2,5-dimethyldecane, and mixtures thereof, more preferably selected from the group consisting of isododecane, isohexadecane, and mixtures thereof.
5. The shampoo composition of any preceding Claim wherein said non-polar volatile solvent is an ether, preferably wherein said ether is selected from the group consisting of isoamyl ether, dipentyl ether, dihexyl ether, and mixtures thereof.
6. The shampoo composition of any preceding Claim wherein the alkyl glyceryl ether sulfonate surfactant comprises alkyl chains derived from at least 50% from alcohols of 10 to 18 carbons, and contains less than 30% diglycerol radicals.

7. The shampoo composition of Claim 1 wherein the hair styling polymer comprises hydrophobic monomer units which are selected from the group consisting of n-butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, t-butyl acrylate, t-butyl methacrylate, and mixtures thereof, preferably wherein the hair styling polymer comprises from 0.5% to 5% of said composition, more preferably wherein the hair styling polymer is selected from the group consisting of t-butyl acrylate/2-ethylhexyl methacrylate, t-butyl methacrylate/2-ethylhexyl methacrylate, and mixtures thereof.

8. The shampoo composition of any preceding Claim which further comprises from 2% to 15% by weight of a secondary surfactant selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, zwitterionic surfactants, and mixtures thereof, preferably wherein said secondary surfactant is an amphoteric surfactant, more preferably wherein said secondary surfactant is a betaine.

9. The shampoo composition of any preceding Claim which further comprises a conditioning agent, preferably wherein said conditioning agent is a cationic polymer, more preferably wherein said cationic polymer is a cationic cellulose and is present at a level of from 0.05% to 1.0% by weight.

10. A method for cleansing and styling the hair comprising the steps of:

- (i) wetting the hair with water,
- (ii) applying an effective amount of the composition of Claim 1 to the hair,
- (iii) shampooing the hair with said composition,
- (iv) rinsing said composition from the hair, and
- (v) drying and styling the hair.

## INTERNATIONAL SEARCH REPORT

 International Application No  
 PCT/US 96/13574

 A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 6 A61K7/50 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)  
 IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 842 850 A (VU) 27 June 1989 see the whole document ---	1-10
A	WO 91 15185 A (PROCTER & GAMBLE) 17 October 1991 see the whole document & US 5 120 532 A cited in the application ---	1-10
A	EP 0 323 715 A (PROCTER & GAMBLE) 12 July 1989 see the whole document -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4842850	27-06-89	NONE	
WO-A-9115185	17-10-91	US-A- 5120532	09-06-92
		AU-A- 7661891	30-10-91
		CA-A- 2079680	07-10-91
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		TR-A- 26319	15-03-95
EP-A-323715	12-07-89	AU-B- 628306	17-09-92
		AU-A- 2678888	15-06-89
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		US-A- 4963348	16-10-90

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<b>(54) Title:</b> CONDITIONING SHAMPOO COMPOSITIONS CONTAINING EMULSION POLYMERIZED POLYMERS  <b>(57) Abstract</b>  Disclosed are shampoo compositions which comprise from about 5 % to about 50 % by weight of an anionic deterative surfactant, from about 0.025 % to about 3 % by weight of an organic, cationic deposition polymer, from about 0.01 % to about 10 % by weight of an emulsion polymerized silicone wherein the polymer is derived from the polymerization of linear dimethylpolysiloxane monomers, and from about 20 % to about 94 % by weight water. The composition provides improved conditioning benefits such as wet and dry combing, and dry hair feel with minimal suppression of the shampoo lather.		



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5                                    **CONDITIONING SHAMPOO COMPOSITIONS CONTAINING**  
   **EMULSION POLYMERIZED POLYMERS**

**FIELD OF THE INVENTION**

10            This invention relates to conditioning shampoo compositions which contain select emulsion polymerized silicone polymers which are derived from the emulsion polymerization of linear dimethylpolysiloxane monomers.

**BACKGROUND OF THE INVENTION**

   Conditioning shampoos comprising various combinations of deterative surfactant and hair  
15   conditioning agents are known. These shampoo products typically comprise an anionic deterative surfactant in combination with a conditioning agent such as silicone, hydrocarbon oil, fatty esters, or combinations thereof. These shampoos have become more popular among consumers as a means of conveniently obtaining hair conditioning and hair cleansing performance all from a single hair care product.

20            While a wide variety of shampoos have been disclosed which contain conditioning aids, they have not been totally satisfactory for a variety of reasons. Cationic conditioning agents are highly desirable for use in hair conditioning due to their abilities to control static, improve wet detangling, and provide a silky wet hair feel to the user. One problem which has been encountered in shampoos relates to compatibility problems between good cleaning anionic surfactants and the many  
25   conventional cationic agents which historically have been used as conditioning agents. Efforts have been made to minimize adverse interaction through the use of alternate surfactants and improved cationic conditioning agents. Cationic surfactants which provide good overall conditioning in hair rinse products, in general, tend to complex with anionic cleaning surfactants and provide poor conditioning in a shampoo context. In particular, the use of soluble cationic surfactants that form  
30   soluble ionic complexes do not deposit well on the hair. Soluble cationic surfactants that form insoluble ionic complexes deposit on the hair but do not provide good hair conditioning benefits, and tend to cause the hair to have a dirty, coated feel. The use of insoluble cationic surfactants, e.g., tricetyl methyl ammonium chloride, can provide excellent anti-static benefits but do not otherwise provide good overall conditioning. Many cationic polymers tend to build up on the hair to result in  
35   an undesirable, "unclean" coated feel. Cationic polymers therefore, conventionally, are preferably used at limited levels to minimize this problem. This, however, can limit the overall conditioning benefits that are obtained. Additionally, cationic conditioning agents commonly do not provide

optimal overall conditioning benefits, particularly in the area of "softness", especially when delivered as an ingredient in a shampoo composition.

Materials which can provide increased softness are nonionic silicones. Silicones in shampoo compositions have been disclosed in a number of different publications. Such publications include  
5 U.S. Patent 2,826,551, Geen, issued March 11, 1958; U.S. Patent 3,964,500, Drakoff, issued June 22, 1976; U.S. Patent 4,364,837, Pader, issued December 21, 1982; and British Patent 849,433, Woolston, issued September 28, 1960. While these patents disclose silicone containing compositions, they also did not provide a totally satisfactory product in that it was difficult to maintain the silicone well dispersed and suspended in the product. Recently, stable, insoluble  
10 silicone-containing hair conditioning shampoo compositions have been described in U.S. Patent 4,741,855, Grote and Russell, issued May 3, 1988 and U.S. Patent 4,788,066, Bolich and Williams, issued November 29, 1988. These shampoo compositions can deliver excellent overall conditioning benefits to the hair while maintaining excellent cleaning performance, even with the use of anionic  
detergent surfactants, for a wide variety of hair types.

15 More recently, improved conditioning shampoos were provided in U.S. Serial No. 07/622,699, Robert L. Wells, filed December 5, 1990, now abandoned, and its continuation application Serial No. 07/778,765, filed October 21, 1991, wherein shampoos containing anionic surfactant, dispersed, insoluble silicone, and certain relatively low ionic strength cationic polymers (greater than about 0.4 meq./gm) were disclosed. These compositions provide excellent hair  
20 cleaning conditioning to a wide variety of hair types, especially including improved conditioning to hair damaged by color treatments, bleaching, permanents, etc.

Japanese Patent Application, Laid Open No. 56-72095, June 16, 1981, Hirota et al. (Kao Soap Corp.) also discloses shampoo containing cationic polymer and silicone conditioning agents. Still other patent publications relating to shampoos with cationic agents and silicone include EPO  
25 Application Publication 0 413 417, published February 20, 1991, Hartnett et al.

Another approach to providing hair conditioning benefits to shampoo compositions has been to use materials which are oily to the touch. These materials provide improved luster and shine to the hair. Oily materials have also been combined with cationic materials in the shampoo formulations. Japanese Patent Application Showa 53-35902, laid open October 6, 1979 (Showa 54-  
30 129135), N. Uchino (Lion Yushi Co.), discloses hair treatment compositions containing cationic polymer, fatty acid salt, and at least 10% of an oily component for use before or after shampooing. Suitable oily components are hydrocarbons, higher alcohols, fatty acid esters, glycerides, and fatty acids. Japanese Patent Application 62 [1987]-327266, filed December 25, 1987, published July 4, 1989, laid open No. HEI 1[1987]-168612, Horie et al., discloses detergent compositions containing  
35 cationic surfactant and/or cationic polymer, anionic surfactant, and specific esters of the formula RCOOR' wherein R and R' are straight or branched chain alkyls.

In spite of these attempts to provide optimal combinations of cleaning ability and hair conditioning, it remains desirable to provide further improved hair conditioning shampoo compositions. For instance, it remains desirable to improve overall conditioning, and especially shine and luster, wet and dry combing, and dry hair feel, of hair treated with shampoo containing  
5 silicone and cationic material. For shampoos containing oily materials in combination with cationic materials, it remains desirable to improve overall conditioning, especially wet combing and detangling, dry combing, and dry hair feel. However merely increasing the level of one or both conditioning ingredients can result in adverse effects such as greasy hair feel and loss of fullness. It is desirable to improve conditioning without suffering from these drawbacks.

10 One attempt to do this is disclosed in WO 95/09599, published April 13, 1995, Murray et al., which is incorporated herein by reference. This patent discloses a shampoo composition containing a cationic polymer deposited in soluble silicone oils, especially dimethiconol. These systems are most effective, e.g., provide uniform deposition of the conditioning agents onto hair, when the silicone is emulsion polymerized and the average particle size of the emulsion polymerized polymer is less than  
15 2 $\mu$ m, preferably less than 1 $\mu$ m.

The addition of silicone oils to conditioning shampoo compositions in the form of aqueous emulsions is known in the art. Conventional silicone emulsion processes include emulsions formed by mechanical shearing of the silicone oil, as well as emulsion polymerization. Both procedures provide emulsion systems in which the particle size of the silicone oils in the emulsion is less than  
20 about 2 $\mu$ m, preferably less than about 1 $\mu$ m, more preferably less than about 0.5 $\mu$ m, even more preferably less than about 0.3 $\mu$ m, even more preferably less than about 0.15 $\mu$ m, and most preferably less than about 0.1 $\mu$ m. The particle size of silicone emulsified oils are typically greater than about 0.01 $\mu$ m.

However, emulsion polymerized silicone emulsions now have inherently provided better  
25 control of particle size in the production of high viscosity fluids and microemulsions. Submicron mechanical emulsions of silicone having a viscosity greater than 60,000 centistokes is very difficult to manufacture. Since emulsion polymerization allows greater ease in the production of viscosities greater than 60,000 centistokes, the industry has migrated toward the use of emulsion polymerization for the production of such high viscosity submicron silicone emulsions.

30 It has now been found that emulsion polymerized silicone emulsions which are made using cyclic silicones can negatively impact lather of conditioning shampoo compositions. However, silicone emulsions derived from the polymerization of linear dimethylpolysiloxanes are able to be added to conditioning shampoo compositions with minimal lather suppression. One hypothesis can be that the residual cyclic silicone leaches from the emulsion phase to the surfactant phase and acts as  
35 an antifoam or soil load, thereby reducing lather performance.

It has also been found that emulsion polymerized silicones wherein the polymer is derived from the polymerization of linear dimethylpolysiloxane monomers having the formula: HO-[Si

(R<sup>1</sup>R<sup>2</sup>)-O-]<sub>n</sub>-H wherein n is greater than about 10 do not exhibit the negative impact on lather of conditioning shampoo compositions. This is achieved because of a higher completeness of the reaction, and the dimethiconol starting material is of sufficient molecular weight to prevent minimal leaching into the surfactant phase.

5 It is therefore an object of the present invention to provide a conditioning shampoo composition for use on hair or skin with improved conditioning performance, and further to provide such a composition with improved uniform deposition of conditioning agents onto hair or skin, and further to provide such a composition which utilizes dimethylpolysiloxane emulsions derived from the emulsion polymerization of linear dimethylpolysiloxane monomers.

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### SUMMARY OF THE INVENTION

The present invention is directed to hair conditioning shampoo compositions which comprise

- (A) from about 5% to about 50% by weight of an anionic surfactant component selected from the group consisting of anionic surfactants, zwitterionic and amphoteric surfactants, said zwitterionic and amphoteric surfactants having an attached group that is anionic at the pH of the composition, and combinations thereof;
- 15 (B) from about 0.025% to about 3% by weight of an organic, cationic, deposition polymer having a cationic charge density of from about 0.2 meq/g to about 5 meq/g and an average molecular weight of from about 5,000 to about 10,000,000;
- 20 (C) from about 0.005% to about 10% by weight of an emulsion polymerized silicone wherein the polymer is derived from the polymerization of linear dimethylpolysiloxane monomers having the formula:



wherein n is from about 10 to about 100, and

- 25 (D) from about 20% to about 94% by weight of water.

### DETAILED DESCRIPTION OF THE INVENTION

The shampoo compositions of the present invention can comprise, consist of, or consist essentially of the essential elements and limitations of the invention described herein, as well any of the additional or optional ingredients, components, or limitations described herein.

30 All percentages, parts and ratios are based on the total weight of the shampoo compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials, unless otherwise specified.

As used herein, the term "soluble" refers to materials that are sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% by weight of the material in water at 25°C. Conversely, the term "insoluble" refers to all other materials that are

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therefore not sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% by weight of the other material in water at 25°C.

As used herein, "nonvolatile" refers to any material having little or no significant vapor pressure under ambient conditions, and a boiling point under one atmosphere (atm) preferably at least about 250°C. The vapor pressure under such conditions is preferably less than about 0.2 mm Hg at 25°C or less, preferably less than about 0.1 mm Hg at 25°C or less.

The shampoo compositions of the present invention, including the essential and some optional components thereof, are described in detail hereinafter.

#### Anionic Detergent Surfactant Component

The shampoo compositions of the present invention comprise an anionic detergent surfactant component to provide cleaning performance to the composition. The anionic detergent surfactant component in turn comprises anionic detergent surfactant, zwitterionic or amphoteric detergent surfactant which has an attached group that is anionic at the pH of the composition, or a combination thereof, preferably anionic detergent surfactant. Such surfactants should be physically and chemically compatible with the essential components described herein, or should not otherwise unduly impair product stability, aesthetics or performance.

Suitable anionic detergent surfactant components for use in the shampoo composition herein include those which are known for use in hair care or other personal care cleansing compositions. The concentration of the anionic surfactant component in the shampoo composition should be sufficient to provide the desired cleaning and lather performance, and generally range from about 5% to about 50%, preferably from about 8% to about 30%, more preferably from about 10% to about 25%, even more preferably from about 12% to about 18%, by weight of the composition.

Preferred anionic surfactants suitable for use in the shampoo compositions are the alkyl and alkyl ether sulfates. These materials have the respective formulae  $\text{ROSO}_3\text{M}$  and  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$ , wherein R is alkyl or alkenyl of from about 8 to about 18 carbon atoms, x is an integer having a value of from 1 to 10, and M is a cation such as ammonium, alkanolamines, such as triethanolamine, monovalent metals, such as sodium and potassium, and polyvalent metal cations, such as magnesium, and calcium. The cation M should be selected such that the anionic detergent surfactant component is water soluble. Solubility of the surfactant will depend upon the particular anionic detergent surfactants and cations chosen.

Preferably, R has from about 8 to about 18 carbon atoms, more preferably from about 10 to about 16 carbon atoms, even more preferably from about 12 to about 14 carbon atoms, in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be synthetic or they can be derived from fats, e.g., coconut oil, palm kernel oil, tallow. Lauryl alcohol and straight chain alcohols derived from coconut oil or palm kernel oil are preferred. Such alcohols are reacted with between about 0 and about 10, preferably from about 2 to about 5,

more preferably about 3, molar proportions of ethylene oxide, and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific non limiting examples of alkyl ether sulfates which may be used in the shampoo compositions of the present invention include sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate, tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, wherein the compounds in the mixture have an average alkyl chain length of from about 10 to about 16 carbon atoms and an average degree of ethoxylation of from about 1 to about 4 moles of ethylene oxide.

Other suitable anionic deterative surfactants are the water-soluble salts of organic, sulfuric acid reaction products conforming to the formula  $[R^1-SO_3-M]$  where  $R^1$  is a straight or branched chain, saturated, aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is a cation described hereinbefore. Non limiting examples of such deterative surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having from about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g.,  $SO_3$ ,  $H_2SO_4$ , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated  $C_{10}$  to  $C_{18}$  n-paraffins.

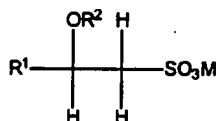
Still other suitable anionic deterative surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil or palm kernel oil; sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil or palm kernel oil. Other similar anionic surfactants are described in U.S. Patent 2,486,921; U.S. Patent 2,486,922; and U.S. Patent 2,396,278, which descriptions are incorporated herein by reference.

Other anionic deterative surfactants suitable for use in the shampoo compositions are the succinates, examples of which include disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; and dioctyl esters of sodium sulfosuccinic acid.

Other suitable anionic deterative surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. In this context, the term "olefin sulfonates" refers to compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid  $SO_2$ , chlorinated hydrocarbons, etc., when used in the liquid form, or by air,

nitrogen, gaseous SO<sub>2</sub>, etc., when used in the gaseous form. The alpha-olefins from which the olefin sulfonates are derived are mono-olefins having from about 10 to about 24 carbon atoms, preferably from about 12 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A non limiting example of such an alpha-olefin sulfonate mixture is described in U.S. Patent 3,332,880, which description is incorporated herein by reference.

Another class of anionic deterative surfactants suitable for use in the shampoo compositions are the beta-alkyloxy alkane sulfonates. These surfactants conform to the formula



where R<sup>1</sup> is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R<sup>2</sup> is a lower alkyl group having from about 1 to about 3 carbon atoms, preferably 1 carbon atom, and M is a water-soluble cation as described hereinbefore.

Preferred anionic deterative surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, and combinations thereof.

Suitable amphoteric or zwitterionic deterative surfactants for use in the shampoo composition herein include those which are known for use in hair care or other personal care cleansing composition, and which contain a group that is anionic at the pH of the shampoo composition. Concentration of such amphoteric deterative surfactants preferably ranges from about 0.5 % to about 20%, preferably from about 1% to about 10%, by weight of the composition. Non limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Patents 5,104,646 (Bolich Jr. et al.), U.S. Patent 5,106,609 (Bolich Jr. et al.), which descriptions are incorporated herein by reference.



Amphoteric deterative surfactants suitable for use in the shampoo composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one  
5 contains an anionic water solubilizing group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Zwitterionic deterative surfactants suitable for use in the shampoo composition are well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can  
10 be straight or branched chain, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. Zwitterionics such as betaines are preferred.

The shampoo compositions of the present invention may further comprise additional surfactants for use in combination with the anionic deterative surfactant component described  
15 hereinbefore. Suitable optional surfactants include nonionic surfactants, cationic surfactants, and combinations thereof. Any such surfactant known in the art for use in hair or personal care products may be used, provided that the optional additional surfactant is also chemically and physically compatible with the essential components of the shampoo composition, or does not otherwise unduly impair product performance, aesthetics or stability. The concentration of the optional additional  
20 surfactants in the shampoo composition may vary with the cleansing or lather performance desired, the optional surfactant selected, the desired product concentration, the presence of other components in the composition, and other factors well known in the art.

Non limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers  
25 and Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Patent 3,929,678, U.S. Patent 2,658,072; U.S. Patent 2,438,091; U.S. Patent 2,528,378, which descriptions are incorporated herein by reference.

#### Deposition Polymer

A deposition polymer is an essential element of the present invention. It will generally be  
30 present at levels of from 0.01 to 5%, preferably from about 0.05 to 1%, more preferably from about 0.08% to about 0.5% by weight. The polymer may be a homopolymer or be formed from two or more types of monomers. The molecular weight of the polymer will generally be between about 5,000 and about 10,000,000, preferably between about 50,000 and about 5,000,000, and most preferably in the range between about 100,000 to about 2,000,000. Preferably the deposition  
35 polymer is a cationic polymer and preferably will have cationic nitrogen containing groups such as quaternary ammonium or protonated amino groups, or a mixture thereof.

The cationic charge density has been found to need to be at least 0.1 meq/g, preferably above 0.5 and most preferably above 0.8 or higher. The cationic charge density should not exceed 5 meq/g, it is preferably less than 3 and more preferably less than 2 meq/g. The charge density can be measured using the Kjeldahl method and should be within the above limits at the desired pH of use, which will in general be from about 3 to 9 and preferably between 4 and 8.

The cationic nitrogen-containing group will generally be present as a substituent on a fraction of the total monomer units of the cationic polymer. Thus when the cationic polymer is not a homopolymer it can contain spacer non-cationic monomer units. Such polymers are described in the CTFA Cosmetic Ingredient Directory, 3rd edition.

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as (meth)acrylamide, alkyl and dialkyl (meth)acrylamides, alkyl (meth)acrylate, vinyl caprolactone and vinyl pyrrolidine. The alkyl and dialkyl substituted monomers preferably have C1-C7 alkyl groups, more preferably C1-C3 alkyl groups. Other suitable spacers include vinyl esters, vinyl alcohol, maleic anhydride, propylene glycol and ethylene glycol.

The cationic amines can be primary, secondary or tertiary amines, depending upon the particular species and the pH of the shampoo. In general secondary and tertiary amines, especially tertiary, are preferred.

Amines substituted vinyl monomers and amines can be polymerized in the amine form and then converted to ammonium by quaternization.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkyl aminoalkyl acrylate, dialkylamino alkylmethacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidine, e.g., alkyl vinyl imidazolium, and quaternized pyrrolidine, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidine salts. The alkyl portions of these monomers are preferably lower alkyls such as the C<sub>1</sub>-C<sub>3</sub> alkyls, more preferably C<sub>1</sub> and C<sub>2</sub> alkyls.

Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C<sub>1</sub>-C<sub>7</sub> hydrocarbyls, more preferably C<sub>1</sub>-C<sub>3</sub> alkyls.

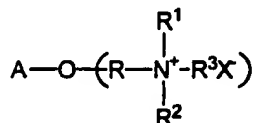
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic deposition polymers include, for example: copolymers of 1-vinyl-2-pyrrolidine and 1-vinyl-3-methyl-imidazolium salt (e.g., Chloride salt) (referred to in the industry by

the Cosmetic, Toiletry, and Fragrance Association, "CTFA" as Polyquaternium-16) such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidine and dimethylaminoethyl methacrylate (referred to in the industry by CTFA and Polyquaternium-11) such as those  
 5 commercially from ISP Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo-and co-  
 10 polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives. Cationic polysaccharide polymer materials suitable for use herein include those of the formula:

15



wherein: A is an anhydroglucose residual group, such as starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups,  
 20 each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup>) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR (trademark) and LR (trade mark) series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide; referred to in the industry (CTFA) as Polyquaternium 10.  
 25 Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200.

30 Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar trade mark series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated by reference herein), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated by reference herein).

The deposition polymer does not have to be soluble in the shampoo composition. Preferably, however, the cationic polymer is either soluble in the shampoo composition, or in a complex coacervate phase in the shampoo composition formed by the cationic polymer and anionic material. Complex coacervates of the cationic polymer can be formed with anionic surfactants or  
5 with anionic polymers that can optionally be added to the composition hereof (e.g., sodium polystyrene sulfonate).

Coacervate formation is dependent upon a variety of criteria such as molecular weight, concentration, and ratio of interacting ionic materials, ionic strength (including modification of ionic strength, for example, by addition of salts), charge density of the cationic and anionic species, pH,  
10 and temperature. Coacervate systems and the effect of these parameters have been described, for example, by J. Caelles, et al., "Anionic and Cationic Compounds in Mixed Systems", *Cosmetics & Toiletries*, Vol. 106, April 1991, pp 49-54, C. J. van Oss, "Coacervation, Complex-Coacervation and Flocculation", *J. Dispersion Science and Technology*, Vol. 9 (5,6), 1988-89, pp 561-573, and D. J. Burgess, "Practical Analysis of Complex Coacervate Systems", *J. of Colloid and Interface Science*,  
15 Vol. 140, No. 1, November 1990, pp 227-238, which descriptions are incorporated herein by reference.

It is believed to be particularly advantageous for the cationic polymer to be present in the shampoo in a coacervate phase, or to form a coacervate phase upon application or rinsing of the shampoo to or from the hair. Complex coacervates are believed to more readily deposit on the hair.  
20 Thus, in general, it is preferred that the cationic polymer exist in the shampoo as a coacervate phase or form a coacervate phase upon dilution. If not already a coacervate in the shampoo, the cationic polymer will preferably exist in a complex coacervate form in the shampoo upon dilution with water to a water:shampoo composition rate ratio of about 20:1, more preferably at about 10:1, even more preferably at about 8:1.

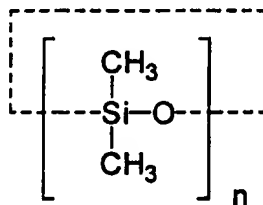
25 Techniques for analysis of formation of complex coacervates are known in the art. For example, microscopic analyses of the shampoo compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phase dispersed in the composition.

30 Preferably the deposition polymer is selected from the group comprising hydroxyalkyl cellulose ethers and cationic guar derivatives. Particularly preferred deposition polymers are Jaguar C13S, Jaguar C15, Jaguar C17 and Jaguar C16 and Jaguar C162. Other preferred cellulose ethers include Polymer JR400, JR30M and JR125.

### Emulsion Polymerized Silicone Polymers

The shampoo compositions of the present invention comprise non-volatile silicone emulsion polymers derived from emulsion polymerization of linear dimethylpolysiloxane monomers. The concentrations of the emulsified silicones generally range from about 0.005% to about 10%, preferably from about 0.05% to about 5%, more preferably from about 0.1% to about 4%, and most preferably from about 0.2% to about 3%. The shampoo compositions preferably comprise dimethiconol. The dimethiconol silicone can either be used as such or it can be end-capped with a further methyl group. The emulsion polymerized silicone can also contain organo-functional groups (amines, esters, quats, etc.). Emulsion polymerized silicones are known in the art, and are disclosed in U.S. Patents 2,891,920, 3,294,725, and 3,360,491, all of which are incorporated by reference herein in their entirety. Emulsion polymerized dimethylpolysiloxane microemulsions are described in E.P. Patent 268,982, which is incorporated herein by reference.

The most common method for emulsion polymerized silicones involves the emulsification of cyclic organopolysiloxanes corresponding to the following formula:



wherein n is from about 3 to about 7, preferably from about 3 to about 5. The emulsified organopolysiloxanes are then polymerized into high viscosity silicone fluids. This process is actually an equilibrium process whereby about 10-15% of the cyclic silicone is left in the emulsion phase.

The shampoo composition of the present invention is preferably substantially free of emulsion polymerized silicones derived from cyclic organopolysiloxanes. As used herein, the term "substantially free" means the composition comprises less than about 1%, more preferably less than about 0.5%, even more preferably less than about 0.2%, even more preferably less than about 0.1% and most preferably less than about 0.05% of emulsion polymerized silicones derived from cyclic organopolysiloxanes.

Another emulsion polymerization method for the manufacture of high viscosity silicone emulsions involves the emulsification of low molecular weight linear organopolysiloxanes corresponding to the formula:



wherein  $\text{R}_1$  and  $\text{R}_2$  are the same or different and are selected from the group consisting of  $\text{CH}_3$ , organofunctional alkyls and alkyl radicals which are linear or branched and have from about 1 to 22 carbon atoms; and n is greater than about 10 to about 100, preferably greater than about 15 to about

100, more preferably greater than about 20 to about 75, even more preferably greater than about 20 to about 50. The linear organopolysiloxane is then polymerized, via condensation reactions, yielding high viscosity silicone polymers.

Without being limited by theory, Applicants believe that emulsion polymerized silicone emulsions which are made using cyclic silicones can negatively impact lather of conditioning shampoo compositions. However, silicone emulsions derived from the polymerization of linear dimethylpolysiloxanes are able to be added to conditioning shampoo compositions with minimal lather suppression. While wishing to not be limited by theory, Applicants further believe that the residual cyclic silicone leaches from the emulsion phase to the surfactant phase and acts as an antifoam or soil load, thereby reducing lather performance. The emulsion polymerized silicone emulsions which are derived from condensation polymerization of polymerization of linear dimethylpolysiloxanes do not exhibit the negative impact on lather of conditioning shampoo compositions due to a higher completeness of the reaction and the starting material is of sufficient molecular weight to prevent leaching into the surfactant phase.

The emulsion polymerized silicone derived from linear low molecular weight organopolysiloxanes of the present invention provide the shampoo compositions with uniform deposition, thereby providing conditioning benefits such as wet and dry combing, and dry hair feel. Moreover the emulsion polymerized silicone derived from linear low molecular weight organopolysiloxanes can be included in the shampoo composition with minimal suppression of the shampoo lather. The average particle size of the emulsion polymerized silicone derived from linear low molecular weight organopolysiloxanes are preferably less than about 2 $\mu$ m, preferably less than about 1 $\mu$ m, more preferably less than about 0.5 $\mu$ m, even more preferably less than about 0.3 $\mu$ m, even more preferably less than about 0.15 $\mu$ m, and most preferably less than about 0.1 $\mu$ m.

#### Water

The shampoo compositions of the present invention are aqueous systems which comprise from about 20% to about 94%, preferably from about 50% to about 90%, more preferably from about 60% to about 85%, water by weight of the composition.

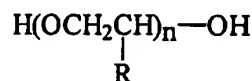
#### Optional Components

In addition to the essential components described hereinbefore, the shampoo compositions of the present invention may further comprise one or more optional components known for use in hair care or personal care products, provided that the optional components are physically and chemically compatible with the essential component described herein, or do not otherwise unduly impair product stability, aesthetics or performance. Nonlimiting examples of such optional components are disclosed in *International Cosmetic Ingredient Dictionary*, Fifth Edition, 1993, and *CTFA Cosmetic Ingredient Handbook*, Second Edition, 1992, both of which are incorporated by reference herein in their entirety. Some nonlimiting examples of such optional components are disclosed below.

**Polyalkylene Glycols**

The shampoo composition may further comprise a polyalkylene glycol to improve lather performance. Concentration of the polyalkylene glycol in the shampoo composition may range from about 0.01% to about 5%, preferably from about 0.05% to about 3%, and more preferably from about 0.1% to about 2%, by weight of the composition.

The optional polyalkylene glycols are characterized by the general formula:



wherein R is selected from the group consisting of H, methyl, and mixtures thereof. When R is H, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, n has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably from about 3500 to about 15,000.

Polyethylene glycol polymers useful herein are PEG-2M wherein R equals H and n has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein R equals H and n has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein R equals H and n has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein R equals H and n has an average value of about 9,000 (PEG 9-M is also known as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein R equals H and n has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

**Suspending Agents**

The shampoo compositions of the present invention may further comprise a suspending agent at concentrations effective for suspending the preferred silicone conditioning agent, or other water-insoluble material, in dispersed form in the shampoo compositions. Such concentrations range from about 0.1% to about 10%, preferably from about 0.3% to about 5.0%, by weight of the shampoo compositions.

Optional suspending agents include crystalline suspending agents which can be categorized as acyl derivatives, long chain amine oxides, and mixtures thereof, concentrations of which range

from about 0.1% to about 5.0%, preferably from about 0.5% to about 3.0%, by weight of the shampoo compositions. These suspending agents are described in U.S. Patent 4,741,855, which description is incorporated herein by reference. These preferred suspending agents include ethylene glycol esters of fatty acids preferably having from about 16 to about 22 carbon atoms. More preferred are the ethylene glycol stearates, both mono and distearate, but particularly the distearate containing less than about 7% of the mono stearate. Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic monoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate. Other long chain acyl derivatives include long chain esters of long chain fatty acids (e.g., stearyl stearate, cetyl palmitate, etc.); glyceryl esters (e.g., glyceryl distearate) and long chain esters of long chain alkanol amides (e.g., stearamide diethanolamide distearate, stearamide monoethanolamide stearate). Long chain acyl derivatives, ethylene glycol esters of long chain carboxylic acids, long chain amine oxides, and alkanol amides of long chain carboxylic acids in addition to the preferred materials listed above may be used as suspending agents. For example, it is contemplated that suspending agents with long chain hydrocarbyls having C<sub>8</sub>-C<sub>22</sub> chains may be used.

Other long chain acyl derivatives suitable for use as suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na, K), particularly N,N-di(hydrogenated) C<sub>16</sub>, C<sub>18</sub> and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Examples of suitable long chain amine oxides for use as suspending agents include alkyl (C<sub>16</sub>-C<sub>22</sub>) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide

Other suitable suspending agents include xanthan gum at concentrations ranging from about 0.3% to about 3%, preferably from about 0.4% to about 1.2%, by weight of the shampoo compositions. The use of xanthan gum as a suspending agent in silicone containing shampoo compositions is described, for example, in U.S. Patent 4,788,006, which description is incorporated herein by reference. Combinations of long chain acyl derivatives and xanthan gum may also be used as a suspending agent in the shampoo compositions. Such combinations are described in U.S. Patent 4,704,272, which description is incorporated herein by reference.

Other suitable suspending agents include carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which description is incorporated herein by reference. Examples of these polymers include Carbopol 934, 940, 941, and 956, available from B. F. Goodrich Company.

Other suitable suspending agents include primary amines having a fatty alkyl moiety having at least about 16 carbon atoms, examples of which include palmitamine or stearamine, and secondary amines having two fatty alkyl moieties each having at least about 12 carbon atoms,



examples of which include dipalmitoylamine or di(hydrogenated tallow)amine. Still other suitable suspending agents include di(hydrogenated tallow)phthalic acid amide, and crosslinked maleic anhydride-methyl vinyl ether copolymer.

Other suitable suspending agents may be used in the shampoo compositions, including those that can impart a gel-like viscosity to the composition, such as water soluble or colloiddally water soluble polymers like cellulose ethers (e.g., methylcellulose, hydroxybutyl methylcellulose, hydroxypropylcellulose, hydroxypropyl methylcellulose, hydroxyethyl ethylcellulose and hydroxyethylcellulose), guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives, and other thickeners, viscosity modifiers, gelling agents, etc. Mixtures of these materials can also be used.

#### Other Optional Materials

Other optional materials suitable for use in the shampoo compositions of the present invention include, but are not limited to, preservatives such as benzyl alcohol, benzoic acid, methyl paraben, propyl paraben, imidazolidinyl urea, iodopropynyl butyl carbamate, methylisothiazolinone, methylchloroisothiazolinone; salts and electrolytes such as sodium chloride, potassium chloride, and sodium sulfate; ammonium xylene sulfonate; propylene glycol; polyvinyl alcohol; ethyl alcohol; pH adjusting agents such as citric acid, succinic acid, phosphoric acid, sodium hydroxide, and sodium carbonate; fragrances and colorings to modify the aesthetic appeal of the composition; hydrogen peroxide; sunscreens agents; hair coloring agents; humectants such as glycerol and other polyhydric alcohols; moisturizers; humectants; anti-oxidants; and chelating agents such as EDTA; anti-inflammatory agents; steroids; topical anesthetics; and scalp sensates such as menthol. Cationic conditioning polymers may also be used in the shampoo compositions.

Synthetic esters may also be used in the shampoo composition to provide improved wet hair feel when used in combination with the essential components of the shampoo composition herein, and in particular when used in combination with the organic conditioning oil described hereinbefore. The concentration of the synthetic esters in the shampoo composition may range from about 0.01% to about 1.0%, preferably from about 0.05% to about 0.5%, more preferably from about 0.08% to about 0.3%, by weight of the composition.

Antidandruff agents may also be used in the shampoo compositions. These agents include particulate antidandruff agents such as pyridinethione salts, selenium compounds such as selenium disulfide, and soluble antidandruff agents. The concentration of antidandruff agents in the shampoo composition may range from about 0.1% to about 4% and preferably about 0.2% to about 2%, by weight of the composition.

Pediculicides can also be used in the shampoo compositions for control of lice infestations. Suitable pediculicides are well known in the art and include, for example, pyrethrins such as those described in U.S. Patent 4,668,666, which description is incorporated herein by reference in its entirety.

### Method of Use

The shampoo compositions of the present invention are used in a conventional manner for cleansing and conditioning hair or skin. An effective amount of the composition for cleansing and conditioning the hair or skin is applied to the hair or skin, that has preferably been wetted with water, and then rinsed off. Such effective amounts generally range from about 1g to about 50g, preferably from about 1g to about 20g. Application to the hair typically includes working the composition through the hair such that most or all of the hair is contacted with the composition.

This method for cleansing and conditioning the hair comprises the steps of:

a) wetting the hair with water, b) applying an effective amount of the shampoo composition to the hair, c) shampooing the hair with the composition, and d) rinsing the shampoo composition from the hair using water. These steps can be repeated as many times as desired to achieve the desired cleansing and conditioning benefit.

### Examples

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. These exemplified embodiments of the shampoo compositions of the present invention provide cleansing of hair and improved hair conditioning performance. Ingredients are hereinafter identified by chemical, trade, or CTFA name.

#### Preparation

The shampoo compositions of the present invention can be prepared by using conventional mixing and formulating techniques. The shampoo compositions illustrated hereinafter in Examples I-XV are prepared in the following manner.

About one-third to all of the total alkyl sulfate surfactant (ammonium laureth-3 sulfate (added as a 25% solution) and/or ammonium lauryl sulfate (added as a 25% solution)) is added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. Cocamide MEA and fatty alcohol, as applicable, are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS), as applicable, is then added to the mixing vessel, and melted. After the EGDS is well dispersed (usually about 5 to 20 minutes) polyethylene glycol and the preservative, if used are added and mixed into the surfactant solution. This mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the ethylene glycol distearate crystallizes to form a crystalline network in the product. The remainder of the ammonium laureth sulfate, lauryl sulfate and other ingredients including the silicone emulsions are added to the finishing tank with ample agitation to insure a homogeneous mixture. A sufficient amount of the silicone emulsions are added to provide the desired level of dimethicone in the final product. Water dispersible polymers are typically dispersed in water as a 1% to 10% solution before addition to the final mix. Once all ingredients have been

added, ammonium xylene sulfonate or additional sodium chloride can be added to the mixture to thin or thicken respectively to achieve a desired product viscosity. Preferred viscosities range from about 2500 to about 9000 cS at 25°C (as measured by a Wells-Brookfield cone and plate viscometer at 15/s).

5

<u>Component</u>	<u>Example Number</u>				
	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>
Ammonium Laurel Sulfate	2	4	4	5	4
Ammonium Laureth-3 Sulfate	8	6	12	10	12
Cocamidopropylbetaine	0	0	2.5	0	1
Jaguar C17 (5)	0.05	0.05	0.05	0.30	0.15
Cocamide MEA	0.5	0.5	0.80	0.80	0
Cetyl Alcohol	0	0	0.42	0.42	0.42
Stearyl Alcohol	0	0	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
EP Silicone (1)	3.0	2.5	3.0	2.0	3.0
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors	----- q.s. to 100% -----				

<u>Component</u>	<u>Example Number</u>				
	<u>VI</u>	<u>VII</u>	<u>VIII</u>	<u>IX</u>	<u>X</u>
Ammonium Laureth-3 Sulfate	9.00	9.00	14.0	14.85	12.50
Cocamidopropylbetaine	1.70	1.70	2.70	1.85	4.20
Polyquaternium-10 (3)	0.05	0.02	0.15	0.15	0.15
Cocamide MEA	0.80	0.80	0.80	0.80	0
Cetyl Alcohol	0	0	0.42	0.42	0.42
Stearyl Alcohol	0	0	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
EP Silicone (4)	3.0	2.5	3.0	2.0	3.0
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors	----- q.s. to 100% -----				

<u>Component</u>	<u>Example Number</u>				
	<u>XI</u>	<u>XII</u>	<u>XIII</u>	<u>XIV</u>	<u>XV</u>
Ammonium Laureth-3 Sulfate	14.0	14.00	14.00	9.00	9.00
Cocamidopropylbetaine	2.70	2.70	2.70	1.70	1.70
Polyquaternium-10 (6)	0.	0.15	0.15	0.05	0.02
Cocamide MEA	0.80	0.80	0	0.80	0.80
Cetyl Alcohol	0	0.42	0	0	0
Stearyl Alcohol	0	0.18	0	0	0
Ethylene Glycol Distearate	0	0	0	1.50	1.50
Carbopol 981 (2)	0.50	0.50	0.50	0	0
EP Silicone (1)	3.0	2.5	3.0	2.0	3.0
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors	----- q.s. to 100% -----				

5 (1) EP Silicone is an experimental emulsion polymerized polydimethyl siloxane of about 97,000 csk with particle size of approximately 300 nm made via linear feedstock available from Dow Corning (2-1520; 13556-34).

(2) Carbopol 981 is a crosslinked polyacrylate available from B.F. Goodrich.

10 (3) Polyquaternium-10 is JR30M, a cationic cellulose derived polymer available from Amerchol.

(4) EP Silicone is an experimental emulsion polymerized polydimethyl siloxane of about 335,000 csk with particle size of approximately 500 nm made via linear feedstock available from Dow Corning (2-1520; PE106004).

15 (5) Jaguar C17 is a cationic polymer available from Rhone-Poulenc

(6) Polyquaternium-10 is JR400, a cationic cellulose derived polymer available from Amerchol.

20 The shampoo composition illustrated in Examples I-XV, all of which are embodiments of the present invention, provide excellent cleansing, lather, mildness, dandruff control (where applicable), and conditioning of hair, especially conditioning and conditioning impression.

## WHAT IS CLAIMED IS:

## 1. A conditioning shampoo composition comprising:

- 5 (a) from 5% to 50%, preferably from 8% to 30%, by weight of an anionic surfactant component selected from the group consisting of anionic surfactants, zwitterionic and amphoteric surfactants, said zwitterionic and amphoteric surfactants having an attached group that is anionic at the pH of the composition, and combinations thereof;
- 10 (b) from 0.025% to 3% by weight of an organic, cationic, deposition polymer having a cationic charge density of from 0.2 meq/g to 5meq/g, preferably from 0.8meq/g to 2.0meq/g, and an average molecular weight of from 5,000 to 10,000,000;
- (c) from 0.005% to 10% by weight of an emulsion polymerized silicone wherein the polymer is derived from the polymerization of linear dimethylpolysiloxane monomers having the formula:
- 15 
$$\text{HO}[\text{Si}(\text{R}^1\text{R}^2)\text{-O}]_n\text{-H}$$
 wherein  $\text{R}_1$  and  $\text{R}_2$  are the same or different and are  $\text{CH}_3$ , or organofunctional alkyls or alkyl radicals which are linear or branched and have from 1 to 22 carbon atoms, and  $n$  is from 10 to 100, preferably greater than 15 to 50; and
- (d) from 20% to 94% by weight of water.

20

2. The composition of Claim 1 wherein the organic cationic deposition polymer is selected from the group consisting of cationic cellulose derivatives, cationic starch derivatives, cationic guar gum derivatives, and mixtures thereof.

25

3. The composition of any one of the preceding claims wherein the composition comprises less than 0.5%, preferably less than 0.2%, of emulsion polymerized silicones derived from cyclic organopolysiloxanes.

30

4. The composition of any one of the preceding claims wherein the emulsion polymerized silicone has an average particle size from 0.01 $\mu\text{m}$  to 2 $\mu\text{m}$ , preferably from 0.01 $\mu\text{m}$  to 0.5 $\mu\text{m}$ .

5. A process for the preparation of a conditioning shampoo composition wherein said process comprises the steps of:

35

- (a) preparing an emulsion polymerized silicone wherein the polymer is derived from the polymerization of linear dimethylpolysiloxane monomers having the formula:



wherein  $R_1$  and  $R_2$  are the same or different and are  $CH_3$ , or organofunctional alkyls or alkyl radicals which are linear or branched and have from 1 to 22 carbon atoms, and  $n$  is from 10 to 100, preferably greater than 15 to 50; and

40 (b) mixing from 0.005% to 10% of the emulsion polymerized silicone with the following components:

- i) from 5% to 50%, preferably from 8% to 30%, by weight of an anionic surfactant,
- ii) from 20% to 94% by weight of water, and
- 45 iii) from 0.025% to 3% by weight of an organic, cationic, deposition polymer.

6. The composition of Claim 5 wherein the organic cationic deposition polymer has a cationic charge density of from about 0.8 meq/g to about 2.0 meq/g.

50 7. The composition of Claim 5 or 6 wherein the organic cationic deposition polymer is selected from the group consisting of cationic cellulose derivatives, cationic starch derivatives, cationic guar gum derivatives, and mixtures thereof.

55 8. The composition of any one of Claims 5, 6, or 7 wherein the composition comprises less than 0.5%, preferably less than 0.2%, of emulsion polymerized silicones derived from cyclic organopolysiloxanes.

9. The composition of any one of Claims 5, 6, 7, or 8 wherein the emulsion polymerized silicone has an average particle size from 0.01 $\mu$ m to 2 $\mu$ m, preferably from 0.1 $\mu$ m to 0.5 $\mu$ m.

# INTERNATIONAL SEARCH REPORT

Int. l. Application No  
PCT/US 97/19273

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/06 A61K7/50

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 432 951 A (UNILEVER PLC ;UNILEVER NV (NL)) 19 June 1991 see the whole document ---	1-4,6,7, 9
X	WO 93 08787 A (PROCTER & GAMBLE) 13 May 1993 see the whole document ---	1,2,6,7
X	EP 0 400 976 A (UNILEVER PLC ;UNILEVER NV (NL)) 5 December 1990 see the whole document ---	1,2,7
X	EP 0 529 883 A (UNILEVER PLC ;UNILEVER NV (NL)) 3 March 1993 see the whole document ---	1,2,7
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Int'l Application No  
PCT/US 97/19273

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